ANISOTROPY IN YIELDING AND FRACTURE TOUGHNESS IN POLYMERS AS AFFECTED BY FORMING AND ANNEALING

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ANISOTROPY IN YIELDING AND FRACTURE TOUGHNESS
IN POLYMERS AS AFFECTED BY FORMING
AND ANNEALING

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NOMENCLATURE

α	die angle
α_e	effective die angle
$\bar{A}_n$	number average molecular weight
$\bar{A}_w$	weight average molecular weight
ABS	acrylonitrile butadiene styrene
β	principal stress ratio
b	notch width on notched tensile specimens
b	indenter thickness, plane strain compression
C	compressive yield strength, absolute value
d	notch depth on notched tensile specimens
Δ	deformation uniformity parameter
$\varepsilon_1, \varepsilon_2, \varepsilon_3$	principal strains in the X1, X2, and X3 directions
ε_f	fracture strain in tension
ε_t	tensile strain
F,G,H,L,M,N	anisotropy parameters
GPC	gel permeation chromatography
h_o	initial sheet thickness
h_1	final sheet thickness
I_1, I_2, I_3	invariants of the stress tensor
J_1, J_2, J_3	invariants of the deviator stress tensor
K_{1C}	plane strain fracture toughness
K_{2C}	plane stress fracture toughness
K_C'	apparent fracture toughness

L	longitudinal Izod sample
NR	notch root radius
MFR	melt flow rate
PC	polycarbonate
PET	polyethylene terepthalate
POM	polyoxymethylene
PP	polypropylene
PS	polystyrene
P	transverse strain ratio
R	transverse strain ratio
R	roll radius
r	rolling reduction
σ_y	yield strength
$\sigma_{Y1},\sigma_{Y2},\sigma_{Y3}$	uniaxial yield strengths in the principal directions
$\sigma_1,\sigma_2,\sigma_3$	principal stresses
t	specimen thickness
T	tensile yield strength, absolute value
θ	notch inclination, grooved tensile bars
γ	shear strain
w	specimen width
X	transverse Izod sample
X1,X2,X3	principal directions in stress space
x	Cartesian coordinate--abscissa
y	Cartesian coordinate--ordinate

SUMMARY

The primary objective of this investigation was to determine experimentally the extent of the effects of anisotropy upon the fracture and yielding behavior of polycarbonate (PC) as a representative of glassy polymers. Anisotropy was developed by cold rolling* and annealing commercially available PC sheet. Portions of the plane stress yield locus were measured by uniaxial tensile tests, grooved tensile tests, and plane strain compression tests. These results were analyzed by the application and extension of Hill's Theory of Anisotropy in Yielding. Fracture behavior was characterized by the Izod impact test with analysis of the observed anisotropy. Material characteristics were determined by gel permeation chromatography (GPC) and melt flow plastometry.

Results show that planar anisotropy was produced in both the fracture and yield behavior of PC sheet by cold rolling. Annealing appeared to have little effect on the relative isotropy of the commercial PC tested.

The fracture behavior of uniformly rolled PC was isotropic in the plane of rolling. However, planar

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*Cold rolling as used in the polymer literature means ambient temperature rolling (i.e. 20-25 C). Cold rolling in metals is defined with respect to the recrystallization temperature range (~0.4-0.5 T_mK).

anisotropy was produced by highly non-uniform cold rolling. Both uniform and non-uniform cold rolling eventually produced ductile fracture behavior. Izod energy levels were at least three to four times those usually observed in as-extruded PC of equal thickness.

The portions of the yield locus that were presented for each processing condition did not all conform to known yield criteria. However, the tensile yield data when combined with the plane strain compression results along with published information indicate that a pressure dependent yield criterion was applicable to PC.

CHAPTER I

INTRODUCTION

1.1 Introduction

Often when dealing with mechanical behavior, the assumption is made that a material is isotropic, i.e. on a macroscopic level various physical properties do not vary appreciably with sample orientation. Certainly in many polycrystalline materials isotropy is often the exception rather than the rule. There are also many instances in practice where anisotropy exists as a consequence of the material processing. A conscious manipulation of the anisotropy in yielding and fracture of a particular material could greatly enhance its suitability for use in many applications and even qualify it for new situations.

Polymers, in particular, have yet to be fully exploited in these areas of property enhancement because the understanding of the yield and fracture mechanisms in many polymers has only come about within the last 10 years. Indeed, the full understanding and application in industry of the physical, thermal, and processing properties of many frequently used polymers is not widespread. Therefore, it was from the approach of a manufacturing or processing engineer (rather than that of the polymer scientist) that this investigation was conducted.

1.2 Objectives

The overall objective of this investigation was to examine polycarbonate with respect to its tensile, compressive, and fracture behavior; and determine the degree of anisotropy in each area brought about by cold rolling and heat treatment.

The specific objectives of the investigation included:

(a) Definition of the degree of anisotropy created in the tensile, compressive, and fracture specimens.

(b) Analysis of the effects of uniform and non-uniform cold rolling (as defined for metals) on the tensile, compressive, and fracture behavior.

(c) Development of plane stress yield loci for the stress conditions imposed on the various tensile and compressive samples by cold rolling and annealing.

(d) Analysis of the empirical yield behavior relative to Hill's Theory of Anisotropy in Yielding and other theories in the literature.

(e) Examination of the effects of uniform and non-uniform cold rolling on the anisotropy of the fracture behavior as measured by the Izod Impact Test.

(f) Examination of the effects of cold rolling and annealing on the thickness transition in the fracture of PC.

(g) Examination of the effects of different notch root radii on the impact behavior of as-extruded, annealed, and cold rolled PC.

(h) Determination of the effects of uniform cold rolling on the molecular weight as measured by Gel Permeation Chromatography.

In addition, several alternative experimental procedures were explored with regard to test techniques and specimen design with the objective of measuring the effects these differences imposed on the results.

1.3 Discussion of the Problem

The fracture behavior of PC (as extruded, cold rolled, and annealed) was explored in the current work by using the Izod notched bar impact test. Impact energy level and the appearance of the fracture surface (ductile, brittle, or mixed mode) were utilized to interpret the effects of the processing and dimension changes on the anisotropy in the fracture behavior of PC.

Anisotropy in the tensile and compressive yield characteristics was examined using uniaxial and plane strain tension tests and plane strain compression tests. Portions of the yield loci were developed from:

(1) the uniaxial and notched tensile tests for first and fourth quadrant principal stress plane points

(2) plane strain compression tests for the third quadrant points.

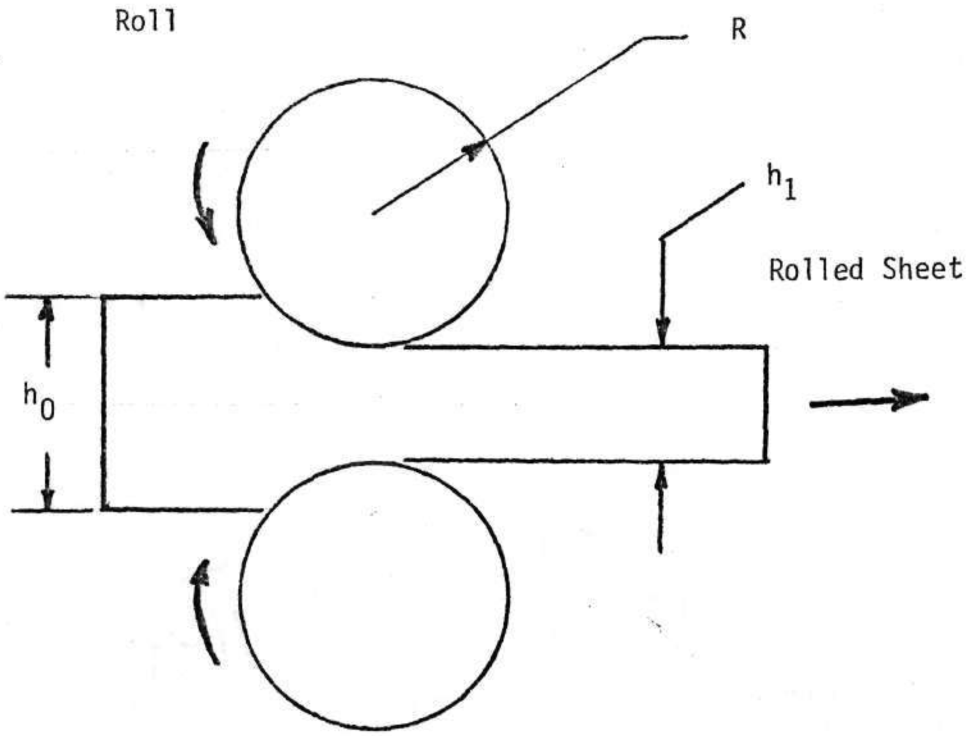
The anisotropic yielding behavior of ductile metals based primarily on the work of Hill [1] served as a benchmark and starting point for this work. The applicability of this theory, or some modification thereof, to the yielding of PC (as a representative of glassy polymers) was one of the objectives of this thesis.

Two closely related problems that had a strong influence on the understanding of the fracture and yielding of PC were the determination of uniformity of deformation distribution in cold rolling and the determination of the degree of anisotropy in the plane of rolling. The uniformity of rolling was assumed to depend on the Δ parameter.

This parameter describes the deformation zone geometry given in Figure 1 and is expressed for plane strain rolling as:

$$\Delta = \sqrt{\frac{h_o}{4Rr}}\ [2-r] \tag{1}$$

Δ values of one or less are associated with fully penetrating deformation such as occurs with thin strip rolling in plane strain while higher Δ values correspond to non-penetrating, modes of deformation. At about Δ=10 the hardness indentation tests are characterized by their low degree of penetration and largely surface effects. A detailed derivation of equation 1 from the general case of parallel non-converging indenters is shown in Appendix 3.



$$r = 1 - h_1 / h_0$$

$$\Delta = \sqrt{h_0 / 4rR}\,(2-r)$$

Figure 1. Deformation Zone and Roll Gap Terminology

In order to define the degree of anisotropy produced in cold rolling or annealing, the concept of transverse strain ratio was adopted from use in describing plasticity in metals. The two transverse strain ratios were defined as follows:

$$R = \frac{\varepsilon_2}{\varepsilon_3} \quad \text{(along X1)} \tag{2}$$

$$P = \frac{\varepsilon_1}{\varepsilon_3} \quad \text{(along X2)} \tag{3}$$

where ε_1, ε_2, and ε_3 were finite true principal strains in the X1 (rolling and extrusion) direction, X2 (transverse planar) direction, and X3 (short transverse or through-the-thickness) direction. Earlier investigations [2,3] found that R in PC tended to increase with tensile strain. To determine R (and P) for the various as-extruded, annealed, and rolled states of PC, an extrapolation of post yield values of R (and P) plotted versus true tensile strain allowed an extrapolation through $\varepsilon_{tensile} = 0$.

Another important consideration was to determine if any morphological changes occurred during the uniform cold rolling. Two different measures of molecular weight were made; one direct--gel permeation liquid chromatography and one indirect--melt flow plastometry.

The fracture specimen design followed the ASTM recommendations [20] for the Izod test with the exception of notch root radius. The effect of variations in the notch root radius were examined as a result of other recent findings [11,12] on this subject.

The design of notched tensile specimens presented a problem because the literature contains different recommendations on the geometric constraints necessary to impose plane strain conditions in the notch. Several notch designs were examined and compared for their effect on the tensile yield results.

Plane strain compression sheet specimens produced third quadrant yield locus measurements, in addition to the first and fourth quadrant information provided by the uniaxial and notched tensile tests. Again, it should be mentioned that this work was approached from the viewpoint of the mechanical or manufacturing engineer rather than that of the polymer scientist and seemingly a degree of rigor was applied (from that viewpoint) that had previously been lacking in the literature on polymers in general and on PC in particular.

1.4 Review of the Literature

Because of its superior physical, processing, and appearance properties relative to other glassy polymers; PC has become a popular engineering thermoplastic for applications requiring quality appearance, rigidity, strength, and toughness. In the 1960's with the rise in popularity in PC commercially, there was a corresponding rise in the investigation of its properties. The approach of most of this prior work has been that of the disciplines of polymer science or chemistry.

1.4.1 Fracture Behavior

The supplier information on PC from the two major sources, General Electric Co., Inc. and Mobay Chemical Co., Inc. [31,32] gave similar impact data on Lexan[R] and Merlon[R] polycarbonates. Figure 2 shows this data and illustrates the thickness transition that was noted throughout the fracture literature on PC. The actual transition thickness using the ASTM [20] Izod test varies between about 0.130 inch and 0.180 inch for as-extruded sheet.

Since the fracture behavior of polycarbonate is claimed to be subject to several parametric transitions (i.e. temperature, thickness, strain rate, thermal history, molecular weight), it was important to survey the literature to note which of these applied in the domain of the current work. This knowledge was deemed essential in designing experimental procedure which would assure valid comparisons.

Legrand [33] evaluated the criterion for the ductile brittle transition in PC in terms of the stress required to propagate a Griffith flaw and the yield stress of the polymer. He found that the density and yield stress for PC annealed at various temperatures were dependent upon previous thermal history and especially molecular weight. He further observed that a flaw formed within the Izod

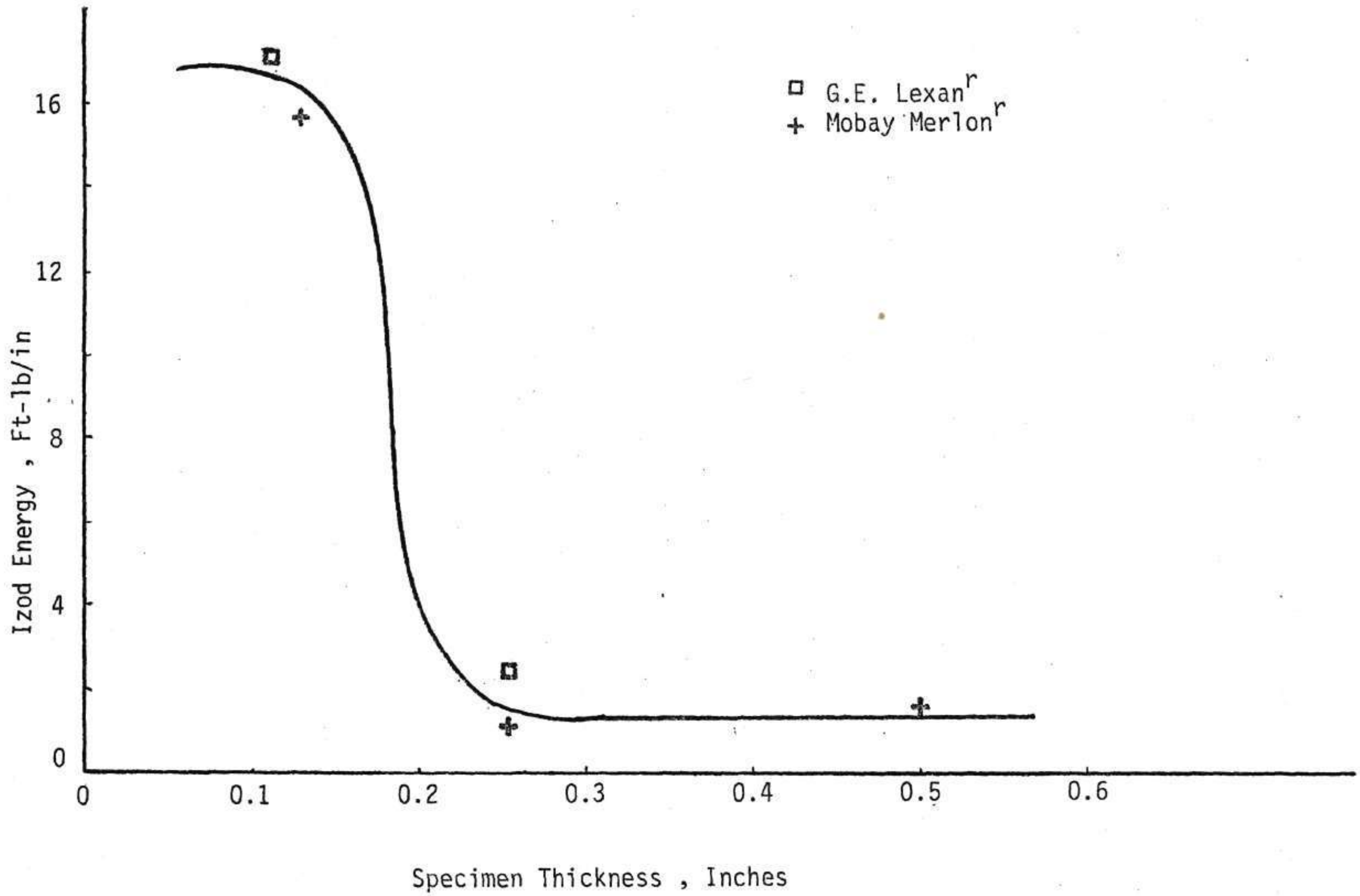


Figure 2. Izod Energy versus As-Extruded Thickness for PC after References 31 and 32

specimen near the notch. If the material surrounding the flaw yielded before a critical size was reached, the flaw became a void and ductile failure resulted. However, if the material surrounding the flaw did not yield, the flaw grew to the critical size for Griffith type crack propagation. The resultant fracture mode was then brittle.

Parvin and Williams [34] investigated the effect of test temperature on the fracture of PC by using single edge notch and surface notch specimens through the range of -120 to 20C. They found a strong thickness dependence in the fracture thoughness which they described in terms of plane strain and plane stress values (K_{C1} and K_{C2}).* These values were insensitive to temperature and strain rate above -40C, but the plane stress values increased at lower temperatures. The independence of both fracture toughness values relative to temperature and strain rate indicated almost no visco-elastic effects in the fracture process. This study was useful to the current work because it allowed variations in test temperature (20-25C) without concern. The lack of viscoelastic effects was qualified by the authors statement "K_C' (apparent fracture toughness) did not show any appreciable rate dependence and the results reported here are all at a

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*Parvin and Williams use K_{C1} for plane strain fracture toughness which is usually denoted in the literature K_{IC}. Their K_{C2} is used for plane stress fracture toughness and should not be confused with K_{IIC}, the mode II fracture toughness. They further define K_C' as "apparent fracture toughness" in terms of K_{C1} and K_{C2}.

cross-head rate of 0.5 inch min^{-1}." Insufficient notch information in this paper precluded strain rate calculation, but it was assumed that Izod test strain rates were several orders of magnitude higher than in these single edge and surface notch specimens. Therefore, independence of fracture behavior of strain rate cannot automatically be assumed.

Johnson, Glover, and Radon [35] carried out fracture toughness* tests on extruded sheets of PC to study variations in K_{1C} with temperature, strain rate, and crack direction. Slow bend and charpy impact tests were used. The variation of K_{1C} with strain rate and temperature was found to be small. Notch acuity was reported to have little effect on K_{1C} values and crack velocity. Specimens having the standard charpy notch produced similar K_{1C} values to those obtained from sharp cracked specimens. They attributed the lack of difference of results obtained using "blunt" and "sharp" notches to the possibility of submicroscopic cracks produced during the machining of the notches. This agreed with Parvin and Williams who noted an approximately constant value for K_{1C} throughout their range of strain rate and temperature.

The division of crack initiation and propagation energy in impact tests on polymers was detailed in the work

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*Johnson et al. used the same nomenclature for fracture toughness as Parvin and Williams which was noted earlier.

of Brown [36] and Elling and Kalish [30]. Brown described a model for the variation of impact strength (charpy) with specimen dimensions. By comparing his model with experiments on several polymers (urethane, PET, PC, and ABS), he was able to decide whether the impact energy went into crack initiation or propagation. He found that crack initiation was the major dissipation mechanism in a number of polymers including razor-notched PC.

Elling and Kalish [30] characterized the fracture behavior of PC in several thicknesses from 1/8 to 1/2 inch using charpy type tests with both the standard notch configuration and a precrack at the notch root. Their results showed that the crack initiation energy was a substantial fraction of the total notched bar energy in brittle conditions but was a small fraction in tough conditions.

Ryan [37] studied the Izod impact and yield properties of PC from two different manufacturers as a function of strain rate, melt flow rate, notch radius, thermal history, and test temperature. He found that both yield stress and the critical molecular weight for the ductile brittle transition increased with strain rate and annealing time. This meant that for PC of a given molecular weight (or melt flow) a progressive increase in the Izod notch acuity would eventually produce brittle fracture behavior.

Similarly, Shea and Cammons [28] determined minimum notch root radii to assure 100 percent ductile failure for nonpigmented PC Izod samples as part of their study of the effects of pigmentation on the impact properties. They found that a 0.003, 0.007, 0.007, and 0.015 inch notch root radius represented the respective minima for 100 percent ductile failures in 1/16, 3/32, 1/8, and 1/4 inch thick PC.

Fraser and Ward [11] examined fracture behavior for PC through a range of notch root radii in the Charpy test. They found that the impact strengths of sharply notched specimens correlated well with the fracture toughness determined in conventional cleavage fracture experiments. Blunt notches also produced constant impact values, but at a much higher level corresponding to a different mode of failure. For the intermediate notch root radii a more complex situation existed that was related to molecular weight.

In brief review of the fracture literature surveyed, it appeared that the ductile or brittle failure in fracture was dependent upon flaw growth, that plane stress fracture toughness (K_{C2}) was independent of temperature above -40C, and that the plane strain fracture toughness (K_{1C}) was essentially constant with respect to temperature and strain rate. Crack initiation was shown to be a significant part of impact energy especially in brittle behavior. Increasing the notch acuity was reported to reduce the impact energy level by shifting the ductile brittle transition to produce brittle behavior and low impact values. It is important to note that the literature listed thus far has suggested that at room temperatures brittle behavior can be induced by the presence of very sharp notches on as-extruded PC impact specimens, sufficient annealing, or sufficiently low molecular weight.

Recent work by Brockway and Shea [12] related the ductile brittle transition in the Izod test to the specimen parameters through dimensional analysis. Design equations were produced using dimensionless parameters relating notch root radius, impact bar thickness, and depth of notch. These equations applied to flame-retardant and non-flame retardant PC at room temperature and in a specified melt flow rate range. These equations were applicable to the current work so that brittle behavior with low toughness will be shown in the as-extruded PC for all thicknesses examined.

Broutman and Krishnakumar [10] examined the effect of thermal treatment on the Izod impact strength of several glassy polymers including PC. By annealing near and above the glass transition temperature (T_g) and quenching to various points below it, they found that the residual stresses created had a great effect on the impact strength. In fact, evidence was presented to show that the thickness transition observed was governed within a range by the residual stresses present and not thickness alone.

Since this effect of residual stress could skew results, part of Broutman's work was reproduced in the current work with one modification (the notch root radius was much smaller).

This will be shown to produce brittle low toughness impact behavior in place of Broutman's tough ductile behavior.

The effects of cold rolling on Izod impact strength of several polymers including PC has been investigated by Broutman [6,9]. In [6] Broutman and Patil examined the stress-strain curves, density changes, thermal stability, hardness and Izod impact strengths of cold rolled ductile amorphous thermoplastic polymers. Among these were PC, ABS, polysulfones, and polyphenylene oxides. Maximum thickness reduction achieved was about 60%. In the case of PC maximum impact strength was obtained at less than 10 percent thickness reduction in rolling, decreased gradually up to the 30 percent reduction level, and then decreased more rapidly at higher reductions. The uniaxially rolled PC was tougher in the transverse direction than in the rolling direction. Broutman [9] concentrated his attention on PC, studying the toughness enhancement caused by cold rolling. He found that improvement in Izod impact strength came at small thickness reduction in rolling. The internal stresses through the thickness of the sheets were studied by birefringence techniques with results suggesting that residual stresses were responsible for impact enhancement rather than molecular orientation.

The primary shortcoming of Broutman's work from the mechanical engineering viewpoint was his lack of consideration for uniformity in cold rolling. This criticism was born out by the Δ analysis of some of his rolling passes and their subsequent effect on the anisotropy in the impact results (see Section 3.5.3). Another aspect of the problem overlooked by Broutman was the effect of cold rolling on the molecular structure. Both melt flow rates (MFR) and molecular weights obtained via gel permeation chromatography were included in the current work as a morphological check.

The combined results of the literature review on as-extruded and annealed PC allowed a valid comparison of the Izod behavior of rolled and unrolled material. This was effected by a conscious effort to design impact specimens that insured brittle low toughness behavior in the as-extruded PC. This also implied that any increase in impact strength observed after processing (rolling or annealing) was attributable to something other than the usual thickness transition.

1.4.2 Tensile Yielding Behavior

The uniaxial tensile behavior of as-extruded PC sheet has been well documented by several sources. Broutman and Patil [6], for example, examined several amorphous thermoplastic polymers, including PC, in both the as-extruded and cold rolled states. The typical stress-strain behavior of PC sheet (as-extruded) is reproduced in Figure 3 from [6]. The yield drop and cold drawing behavior noted in Figure 3 is typical of as-extruded PC and several other polymers such as ABS, polysulfones, polyphenylene oxide, and PVC.

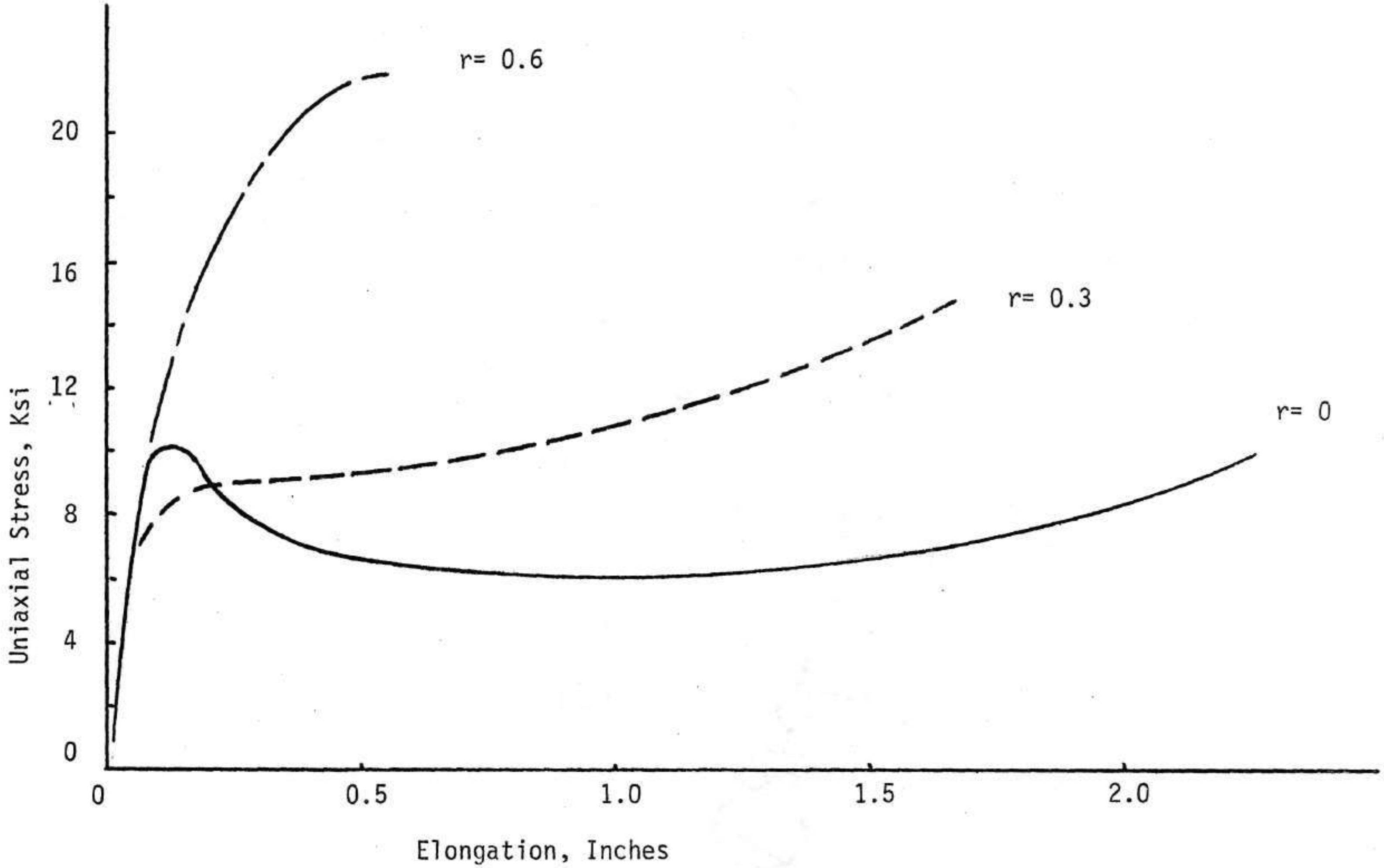


Figure 3. Typical Uniaxial Stress-Elongation Behavior of As-Extruded and Cold Rolled PC after Broutman and Patil, Reference 6

The cold rolled PC showed the effects of rolling in the uniaxial stress-strain behavior. The yield strength in the X1 (extrusion and rolling) direction was depressed below as-extruded levels at rolling reductions up to about 0.30. Rolling reduction is defined as:

$$r = 1 - \frac{h_1}{h_0} \tag{4}$$

where

h_1 = final thickness

h_0 = initial thickness

At greater rolling reductions (0.40 to 0.60) the yield strength was greater than the as-extruded values. In the planar transverse direction (XZ), the cold rolled PC showed a definite depression in yield strength below as-extruded levels. It did not recover (as did the X1 yield strength) nor exceed the as-extruded yield strength at greater degrees of rolling.

Murray and Rusch [4] observed the effect of cold rolling on the tensile behavior of PC over the temperature range -60C to +100C and a strain rate range $1\text{x}10^{-2}$ to $1\text{x}10^{2}$ %/sec. Cold rolling was found to have profound influence on the mechanical properties of PC. At 60C (the nearest experimental point to room temperature), the tensile test results were parallel to Broutman's with the cold rolled uniaxial yield strength greatest, followed by the as-extruded, and the transverse planar values at all strain rates examined.

Bahadur and Henkin [7] examined uniaxial tensile behavior of polymer sheets (acetal, nylon 66, PVC, and PC) cold rolled at room temperature to varying amounts of cold work in a "conventional two-mill roll." They found that yield strength for PC increased with increasing cold work except for a slight drop at low values of cold work. Bahadur and Henkin [7] stated that the rolling reduction steps selected were small so as to ensure uniform deformation and avoid excessive heating during the cold rolling operation. The use of small reduction steps had just the opposite effect; concentrating deformation near the roll surface and promoting non-uniform (non-penetrating-high Δ) deformation. A point of confusion pertaining to precisely what constituted "uniform deformation" is common to the literature on cold rolled polymers. As was noted in Section 1.4.1, Broutman [6,9] and others did not consider uniformity in rolling deformation as it is defined for metals (Δ parameter) and as is used in the current work. When non-uniform deformation was present in experimental material, valid comparisons could not be drawn because of differences in residual stress patterns or differences in molecular orientation mentioned by the above author. This was found in the current work to be more important in the fracture behavior than in the tensile behavior.

The effect of cold rolling on the morphology of PC was considered in the literature primarily in terms of density changes. Density increases were reported in the range of 0.08 percent by Bahadur and Henkin [7] up to 0.251 percent by Broutman and Patil [6]. A significant variation in density was found depending on where in the sheet cross section the investigators removed their samples. This might have been due to the non-uniform deformation that was inadvertently built into their experiments.

Although significant (1-2%) density decreases have been demonstrated on crystalline or semi-crystalline polymers that have been cold rolled, amorphous polymers and PC in particular show little change in density as shown above. For this reason the current work did not include density measurements. In place of density, it will also be seen that morphology was to be characterized in the current study by gel permeation chromatography (GPC) and melt flow plastometry (Section 2.8).

One of the important features of the current work has been to define the degree of anisotropy in the plane of the sheet PC caused by rolling or annealing. As a starting point, the work of Hill was chosen because it was regarded as a primary source in anisotropy and yielding of metals. Hill [1] developed a theory which described, on a macroscopic scale, the yielding and plastic flow of an anisotropic metal. A yield criterion was postulated on general grounds for isotropic metals and contained six anisotropy parameters to specify the state. The theory was applied to the data from thin uniaxial tensile specimens from rolled sheet after Korber and Hoff [38]. These data supported Hill's theory of yielding and demonstrated two equally possible necking directions whose orientation depended upon the angle between the specimen strip axis and the rolling direction. Manipulations of and assumptions pertaining to Hill's theory are clarified by Backofen [15] (see Appendix 4 for further discussion of Hill's theory).

It will also be seen that in order to obtain first and fourth quadrant yield locus measurements on PC, it was decided to adopt notched or grooved tensile specimens from Hill [8]. In 1953, Hill [8] discussed the use of obliquely notched or grooved strips to obtain plane strain conditions and a long narrow zone of distortion represented by the notch in tension. Using the segment displacement angle (for notches other than 90° to the tensile axis) and the measured load, the yield criterion under any state of combined stress was deduced. This method was derived for ductile metals but was later applied to both metals and polymers. Hill's constraints (Figure 4) have been followed in the current work with the exceptions discussed in Section 3.3.

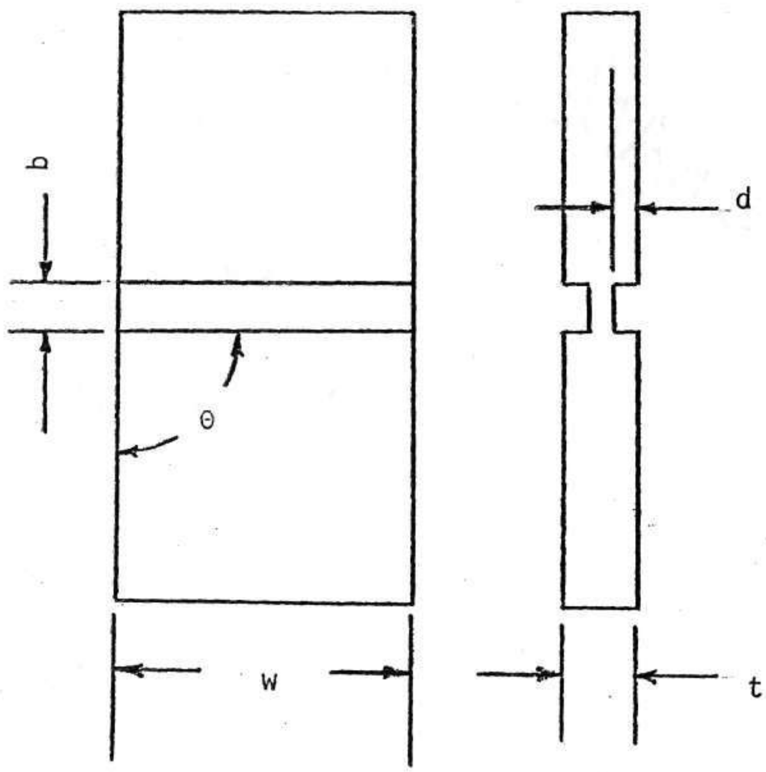
Among those studies involving polymers were Lee [13] and Higuchi and Hyakutake [14]. Lee applied obliquely grooved sheet samples to the tensile study of rubber-modified polystyrene (PS) to establish conditions that led to the early stage of plastic deformation under combined stress loading. By applying plasticity theory and Hill's method portions of the principal stress yield locus were measured for rubber-modified polystyrene. Hill's constraints were followed (Figure 4) with the exception of w/b which was about one-third of Hill's recommendation.

Higuchi and Hyakutake [14] investigated the mechanical behavior of annealed PC and determined a necking criterion. Tests of several loading conditions (tension, compression, torsion and internal pressure tests of thin-walled cylinders) were carried out at room temperature. The mechanical properties were compared with one another in terms of equivalent stress and strain. The notched tensile samples were used to determine first quadrant yield locus points in the principal stress plane. Hill's constraints were suggested on these samples but not expressly stated.

1.4.3 Plane Strain Compression Behavior

To obtain more extensive information on the yield locus, plane strain compression tests are included in the current work. Third quadrant points are valuable in suggesting the pressure dependence of the yield criterion.

Miles and Mills [2] examined the theory of deep drawing for thermoplastics. Orientation hardening after initial yielding and ease of crack formation were shown to change the usual correlation between the drawability of the sheet and the low strain plastic behavior of the material.



Hill's Constraints	Lee's Constraints
$w/b \geq 20$	$w/b = 8$
$t/d \leq 6$	$t/d = 3.3$
$b > t-2d$	$b > t-2d$
$\Theta = 90$	$\Theta = 90$

Figure 4. Plane Strain Notched Tensile Specimen with Dimensional Constraints after Hill and Lee, References 8 and 13

Attempts to improve the limiting draw ratio of thermoplastics by biaxially rolling the sheet prior to forming were shown to be effective only if the polymer did not craze easily under tensile stresses. In the definition of the limiting draw ratio, the plane strain compression values were required. Throughout these tests, stress-strain information on PC sheet in plane strain was presented for both unrolled, annealed PC and biaxially rolled PC.

Backofen [15] has also suggested dimensional constraints necessary to impose plane strain in an indentation compression test. With these two sources, plane strain compression was studied in the current work.

1.4.4 Summary

In summary, the fracture literature reviewed has detailed the growth of flaws and their role in ductile and brittle failure (for example Legrand [33]). The effects of various parameters on the ductile brittle transition and on fracture toughness were discussed by Parvin and Williams [34] and Johnson et al. [35] for test temperature, strain, crack direction and notch acuity. Brown [36] and Elling and Kalish [30] demonstrated that a substantial portion of the impact energy in fracture appears to be dissipated in crack initiation.

Both Ryan [37] and Shea and Cammons [28] determined that smaller Izod notch root radii shifted the ductile brittle transition to smaller sample thicknesses. This was further confirmed experimentally by Fraser and Ward [11] and theoretically by Brockway and Shea [12] who related the ductile brittle transition in the Izod test to the specimen parameters through dimensional analysis.

The effects on the transition thickness of residual stresses developed by annealing and quenching PC were reported by Broutman and Krishnakumar [10]. They found that these residual stresses governed the thickness transition in certain thickness ranges.

Broutman [6,9] in examining the effects of cold rolling on the Izod impact strength found that toughness enhancement occurred at small rolling reductions in thickness (less than 10%). Residual stresses were suggested as the cause for the increased toughness via birefringence measurements. Lack of uniformity in the cold rolling process, however, made the comparisons and conclusions suspect.

Uniaxial tensile specimen behavior of as-extruded and cold rolled PC as well as other polymers was studied by Broutman and Patil [6] and Murray and Rusch [4]. Anisotropy in the yielding behavior was noted with samples taken in the X1 (rolling and extrusion) direction being stronger than those of the X2 direction. The X1 yield strength was initially depressed by rolling but recovered to greater than as-extruded values at the higher rolling reductions. The X2 values remained below the as-extruded level throughout the cold rolled material. Similar results were obtained by Bahadur and Henkin [7].

The degree of anisotropy in the yielding behavior of an anisotropic metal was explored by Hill [1]. The use of notched or grooved tensile specimens was developed by Hill [8] for application to ductile metals. With this method, portions of the principal stress plane yield locus were developed. Later applications to metals and polymers (see Table 8) were successful. Among the polymer studies was the work of Lee [13] who applied the obliquely grooved strips to rubber-modified PS and produced yield locus measurements in the first and fourth quadrants. Higuchi et al. [14] used these specimens in the study of annealed PC to determine first quadrant yield locus information.

The tensile yield literature detailed the study of cold rolling and annealing applied primarily to uniaxial specimen behavior. The notched tensile behavior of PC has been investigated in the as-extruded and annealed condition to some limited extent. Both the material used in previous fracture studies as well as that used in the yielding studies which had been subject to cold rolling, was in fact rolled in a somewhat non-uniform manner.

Following Miles and Mills [2] and Backofen [15] the plane strain compression test results (for PC) and the dimensional constraints (for metals) may be elucidated. The plane strain compression results provide third quadrant yield locus data which is important in the discussion of pressure dependence in the yield criterion.*

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*Yield criteria for polymers are discussed in Appendix 4.

CHAPTER II

EXPERIMENTAL PROCEDURE

2.1 Experimental Plan

The basic experimental plan was based on several material property tests designed to determine the extent of anisotropy effects on the tensile, compressive, and fracture behavior produced by cold rolling and annealing an as-extruded PC sheet. Several configurations and thicknesses of uniaxial tensile samples allowed determination of the yield and strain behavior such that the basic uniaxial tensile test points on the plane stress yield locus could be fixed.

Notched tensile specimens allowed the imposition of plane strain conditions within the notch. By varying the angle θ (Figure 4), different stress states were produced in the notch which correspond (theoretically), at yield, to further specific plane stress points on the yield locus. In order to obtain additional information for the various yield loci and also to further investigate the effect of the hydrostatic component in the yielding behavior of PC, plane strain compression tests were conducted on various sheet samples.

By straining uniaxial tensile specimens beyond yielding and noting the width and thickness reduction, an approximation of the transverse strain ratios (R and P) was made by linearly extrapolating the resulting R or P vs true tensile strain (ε_t) curves back to zero strain. The impact behavior was measured for various thicknesses of PC combined with differing degrees of uniform and non-uniform cold rolling or heat treatment in order to establish the effect of anisotropy on the fracture behavior. The appearance of the resulting fracture surfaces was also used to make observations concerning the as-extruded PC and of the effects of subsequent processing.

The effects of cold rolling on the molecular structure of PC were quantified directly from Gel Permeation (liquid) Chromatography (GPC). This analysis provided both number average ($\bar{A}_n$) and weight average ($\bar{A}_w$) molecular weights. An in-depth analysis of the information from all these tests permitted the construction of an interesting picture of the anisotropic behavior of annealed or cold rolled PC.

2.2 Processing and Test Equipment

The PC sheets were rolled on a Stanat model F 100, 7.5 HP 3 in x 5 in, 2 high rolling mill, with all passes performed dry (unlubricated) and in the prior extrusion direction at about 22 feet per minute. All tension and compression tests were performed on a closed loop model 1251 Instron Testing Machine (cross head speed range 0.0004 in/min to 7.8 in/min) with load monitoring and tensile strain measurement using a 1 in gauge length 50% deformation type extensometer. Impact tests were run on an Izod-Charpy swinging hammer impact tester built by Wiedemann-Baldwin from a Bell Laboratories design. Several energy ranges were available to the experimenter by adjusting the weight of the swinging hammer.

Material structural properties were examined by the use of the Waters Model 440 Gel Permeation Liquid Chromatograph for molecular weight determination and a Tinius Olsen Thermodynae plastometer for melt flow values.

All sample annealing was conducted in a Blue M Model ESP 400 forced air oven with temperature control and optional one pass or recirculating air. Temperatures were monitored with a Stow Lab PS 921 electronic thermometer.

2.3 Material Tested

The material used throughout this work was an extrusion grade Lexan^R polycarbonate as produced in extruded sheets (4 ft x 8 ft as-purchased) of 1/8 in, 3/16 in, 1/4 in, and 1/2 in nominal thickness. Actual thicknesses were approximately 0.120 in, 0.180 in, 0.243 in, and 0.475 in, respectively, as produced by Rowland Products, Inc., Kensington, Connecticut; marketed directly under the name Rowland and also Tuffak^R; and distributed by Rohm and Haas, Philadelphia, Pennsylvania.

Lot or batch numbers were not available, but direct discussions with the engineering manager of Rowland established how the material was processed. The resin used to melt extrude the sheets of PC was carefully dried above 100C so that moisture entrapment was minimized. The resin was then extruded to fabricate a continuous sheet which was quench cooled in-line in cold water to near room temperature. The large continuous sheet was air dried, coated with a non-stress cracking adhesive backed paper (identification information is read in the extrusion direction) and cut to size (commonly 4 ft x 8 ft).

2.4 Experimental Procedure: Tensile Tests, Uniaxial and Notched Specimens, on As-Extruded Annealed, and Cold Rolled PC

Samples of as-extruded 1/4 in (nom) thick PC were carefully machined at high cutting tool speed and low feed rate (approximately 700 SFPM) using no lubricant (to avoid stress cracking) to produce test pieces shown in Figure 5. These plane strain tensile specimens had dimensional relations specified by Hill shown earlier in Figure 4.

In the as-extruded form two samples each were machined with $\theta = 90°$, $75°$, $55°$, and $30°$. The samples with $\theta \neq 90°$ used the cross notch shown in Figure 5b. This series of specimens was designated as the M-series. The notch angles were chosen to locate several first and fourth

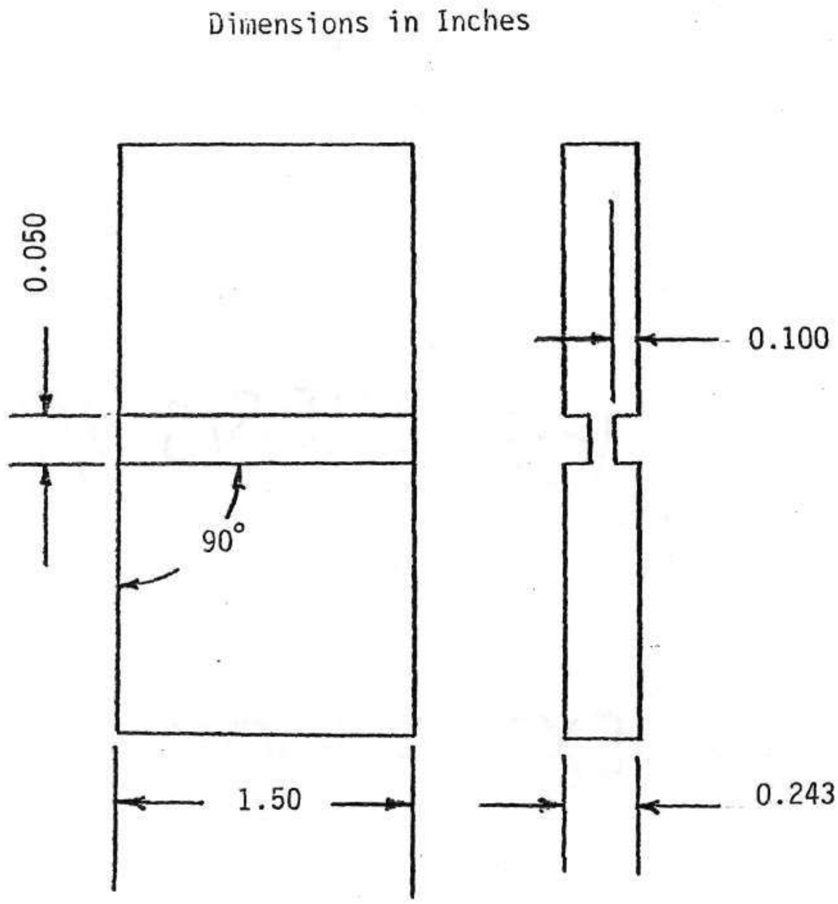
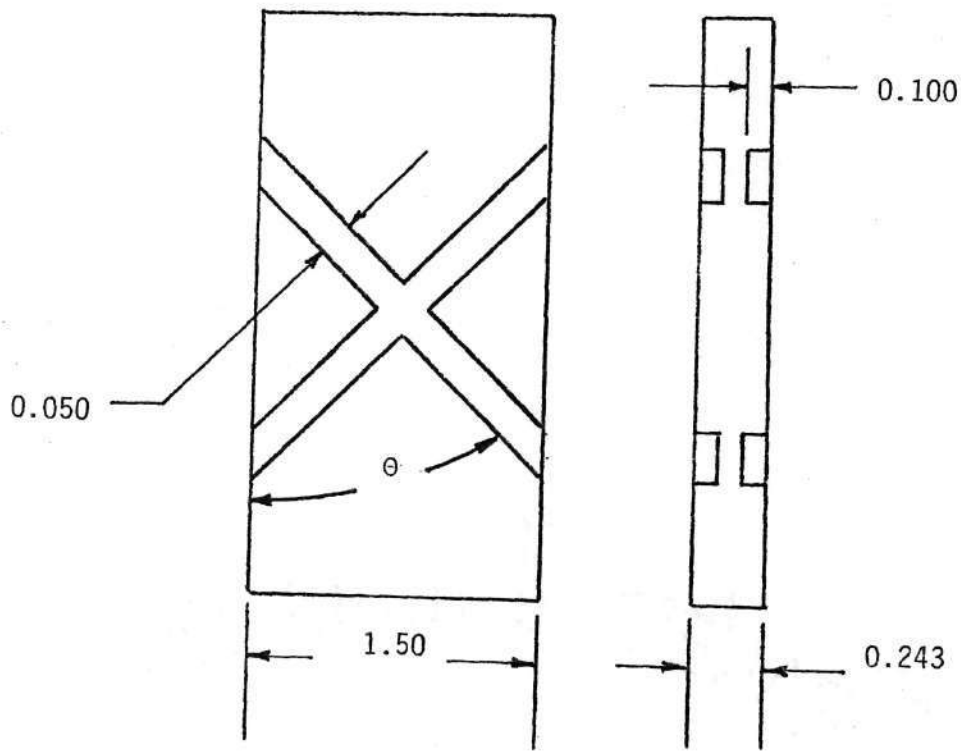


Figure 5a. Plane Strain Notched Tensile Specimen Dimensions - 1/4 Inch As-Extruded PC, $\Theta = 90^\circ$

Dimensions in Inches



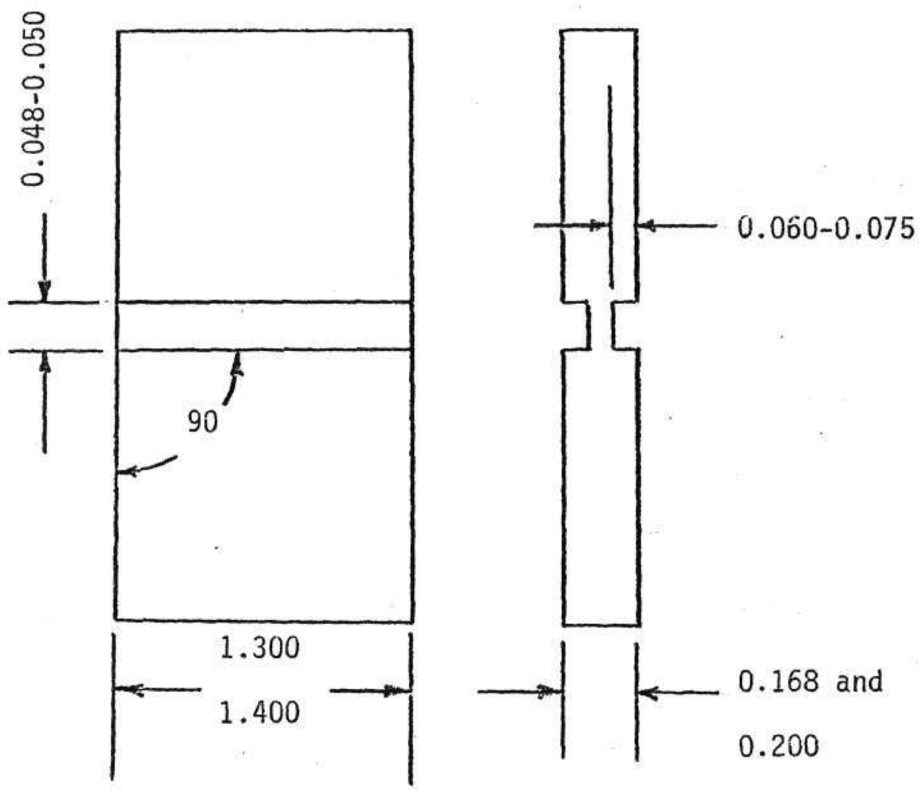
Θ= 30, 55, 75 degrees

Figure 5b. Plane Strain Notched Tensile Specimen Dimensions - 1/4 Inch As-Extruded PC, Θ ≠ 90°

quadrant points on the plane stress yield locus of as-extruded PC.

Cold rolled samples of the originally 1/4 in PC were produced in the T-20 and T-30 series with $\theta = 90°$. Three samples each of uniformly rolled PC ($\Delta<1$) were produced using Figure 6 dimensions. The total amount of rolling reduction r from equation (4) was approximately 0.18 and 0.30 respectively. Uniaxial tensile specimens were also machined from as-extruded and cold rolled 1/4 in PC (Figure 7). In order to make comparison in gauge thickness between the notched and uniaxial samples, the sheets that the uniaxial samples were taken from were "cored." This means the same material that is measured in the gauge thickness of the notched samples was approximated in the uniaxial test samples by removing material from both surfaces of the PC down to nearly the same thickness as the notch. These 'cored' uniaxial tests were undertaken for the as-extruded, cold rolled, and annealed PC in order to minimize any inherent through-the-thickness differences between thin and thick gauge sections. The annealed notched tensile specimens were machined from the dimensions in Figure 6a and tested in both the as-extruded and annealed conditions (3 each) with $\theta = 90°$ and $45°$.

All dimensions in all samples were measured to the nearest 0.0005 inch with a standard one inch Vernier barrel micrometer or dial indicating Vernier caliper (inside and



Dimensions in inches

Figure 6a. Plane Strain Notched Tensile Specimen Dimensions-Cold Rolled, h_0 =1/4 inch PC

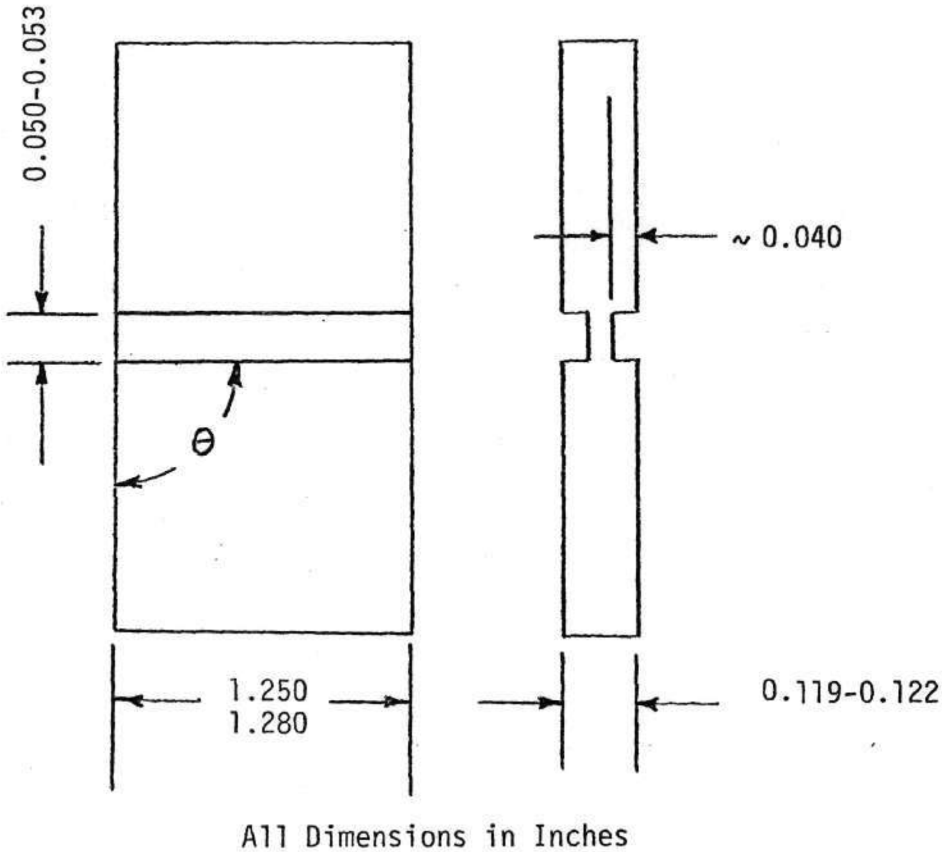
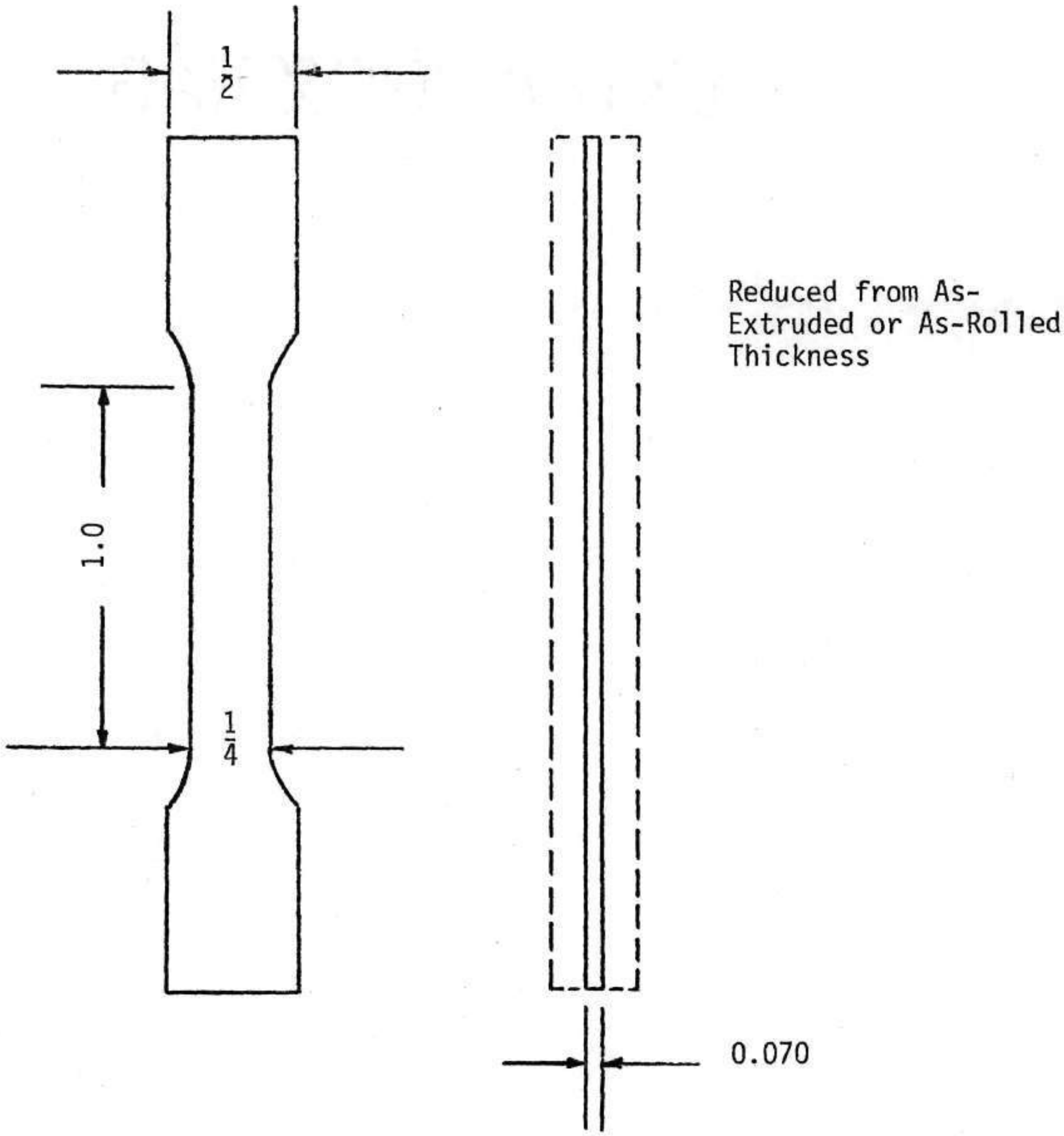


Figure 6b. Plane Strain Notched Tensile Specimen Dimensions- Annealed, h_0 = 1/4 inch PC



All Dimensions in Inches

Figure 7. Reduced Thickness Uniaxial Tensile Specimens - As-Extruded,Cold Rolled, and Annealed PC

outside). The tensile specimens were run in random order within a group (i.e. notched tensile or uniaxial test) on themodel 1251 Instron tensile testing system with a crosshead speed that produced a strain rate of approximately 0.8 to 1.0 min^{-1}. This meant a crosshead speed of approximately 1 mm/min (approximately 0.040 in/min) for the notched tensile tests (with an approximate 0.050 in gauge length) and about 20 mm/min (approximately 0.8 in/min for the uniaxial tests (with an approximate 1.0-1.09 inch gauge length). The chart speed was governed by the strain signal generated by the attached extensometer. Full scale chart deflection was 250, 500, or 1000 lb depending on the type of sample and degree of processing. For each specimen a load-strain chart was produced and the 0.5%, 1.0%, 2.5%, and maximum load offsets were drawn parallel to the linear elastic strain range. The results of the uniaxial and notched tensile tests allowed the construction of portions of yield loci based on the stress ratios (σ_1/σ_Y) at the several offsets in the as-extruded samples plus comparison with established and postulated yield criteria. The cold rolled PC samples allowed comparison between the uniaxials and one plane stress tensile quadrant point ($\theta = 90°$).

The annealed samples allowed comparison between the uniaxial yield test results and two plane stress points: one in the first quadrant ($\theta = 90°$) and one in the fourth quadrant ($\theta = 45°$). In addition to determining experimentally parts of the yield loci, some of the uniaxial test specimens were further tested to determine the extent of anisotropy produced by cold rolling.

Uniaxial samples taken from both the X1 and X2 directions in the r = 0, r = 0.18 and r = 0.30 cases were strained past the yield point in tension. In the as-extruded case, the load drop was accompanied by a neck formation. In such cases, the crosshead was stopped immediately. This was followed by width and thickness measurements in the neck to the nearest 0.001" and tensile strain measurement based on the elongation of a premeasured gauge length. After these micrometer measurements, the crosshead was restarted at 20 mm/min (~0.8 in/min) for about 5 seconds, stopped, and the measurements repeated. This sequence proceeded until theneck commenced cold drawing, i.e. the width-thickness ratio remained constant. Post yield measurement on the cold rolled uniaxial test bars began immediately after the load drop, as there was no neck formation and the gauge section reduced its width and thickness dimensions uniformly. Again, the sequence proceeded until there was sufficient data (at least three points) to attempt an extrapolation.

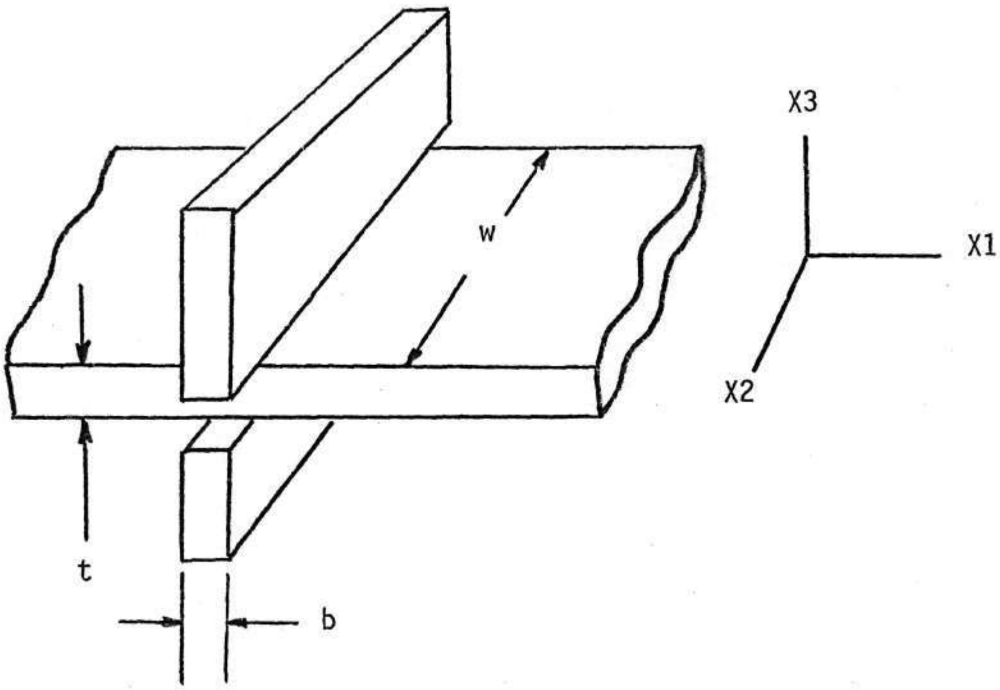
From all these data, R and P values for the PC sheet were obtained by extrapolating the R or P versus true tensile strain (ε_t) back through $\varepsilon_t = 0$ for each processed condition (r = 0, r = 0.18, and r = 0.30). Data points for the isotropic case (R = 1.0) were plotted in the X1-X2 principal stress plane and compared to yield loci appropriate to metals (e.g. VonMises) and polymers (pressure dependent criteria from [22]) by employing an isotropic yield criterion for plane strain conditions in the notched samples after Backofen [15] (see Appendix 4). The cold rolled PC samples provided one plane stress point (θ = 90°) to plot in the X1-X2 plane. It was also determined by the stress ratio σ_1/σ_y (for X1) and by Backofen [15] that:

$$\beta = \frac{\sigma_2}{\sigma_1} = \frac{R}{R+1} \qquad (5)$$

for plane conditions. The isotrpic theory was applied to the annealed notched tensile data for the X1-X2 plane in the same manner as the as-extruded case.

2.5 Experimental Procedure: Plane Strain Compression Tests on As Extruded and Cold Rolled PC

Sheet stock samples of 1/4 in thick PC were selected as-extruded and cold rolled. In order to achieve plane strain compression, the dimensional relationships between indenters and sample shown in Figure 8 according to Backofen [15] were followed. These compression tests were run on the Model 1251 Instron Testing System with a crosshead speed of 1 mm/min (~0.040 in/min) and a chart speed of 100 mm/min (~4.0 in/min). The indenters appear in Figure 9 and were

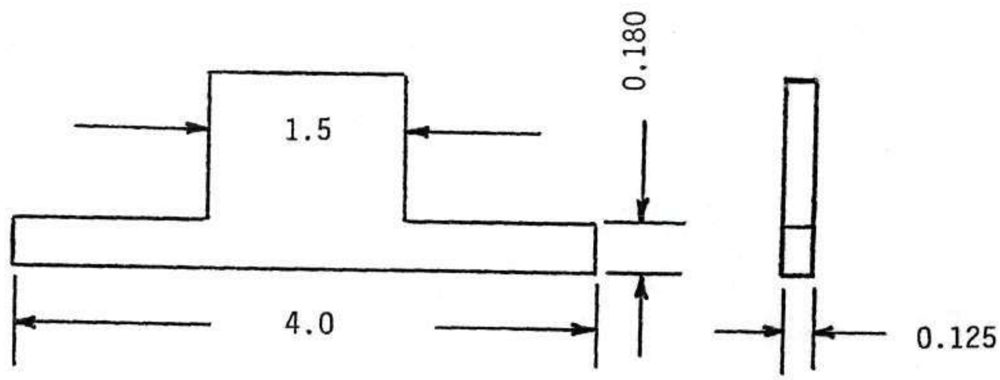


Backofen's Constraints

$w/t \geq 10$ $b/t \leq 3$

Figure 8. Plane Strain Compression Indenter and Specimen Dimensional Constraints after Backofen, Reference 15

Dimensions in Inches



Material: AISI 1020 Steel

Not to Scale

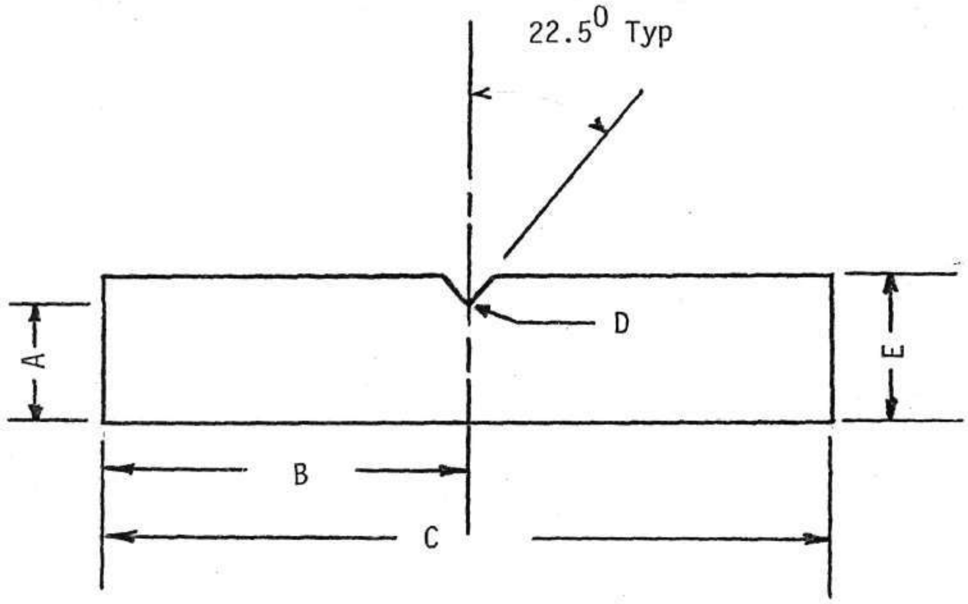
Figure 9. Plane Strain Compression Indenter Dimensions

used dry and unlubricated. The sheet thickness varied with degree of processing while the sheet width was approximately 2.75-3.00 inches. Full scale chart deflection was 5000 lb and examination of the resulting load-displacement charts allowed discussion of the stress-strain behavior.

2.6 Experimental Procedure: Izod Impact Tests on As-Extruded, Annealed, and Cold Rolled PC

PC sheet stock in 1/8 in, 3/16 in, 1/4 in, and 1/2 in (all nominals) was selected for Izod impact specimen preparation (per ASTM-256-72a [20]). The 1/4 in material was the very same used in the tension and compression work. In the as-extruded condition all samples (3 longitudinal, 3 transverse from each thickness) had standard Izod dimensions in all respects including the notch tip radius (0.010 in ± 0.002 in) (Figure 10 from [20]).

Preliminary work with the cold rolled PC plus recent findings in the literature [11,12] led to the use of a 0.002 in notch tip radius for the rest of the impact studies. The notches, in all cases, were cut on a custom scientific instrument fly cutter with a feed rate of 0.050 in/min and cutter rotational speed of 416 RPM (~490 surface feet/min). The 0.002 in tip radius was chosen as it represents the lower limit of radius for standard cutting tools. A smaller radius is possible by some special techniques, but the pressures exerted on these finer tool tip radii during the



A= 0.400 ± 0.002 inch

B= 1.260 +0.000 -0.002 inch

C= 2.500 +0.000-0.010 inch

D= 0.010 or 0.002 inch

E= 0.500 ± 0.006 inch

Thickness= 0.119 through 0.475 inch

Figure 10. Izod Impact Specimen after Reference 20

notch cutting process tend to blunt them rather quickly back into the 0.001-0.003 in range.* The notching process was water cooled with a water temperature of approximately 55F (13C). Cold rolling was possible only on 1/4 in PC and below due to the roll gap limitations on the Stanat mill on which both uniformly and non-uniformly rolled samples were produced. Annealed Izod samples with pre and post anneal notches applied were also tested. In most instances (except where noted) each experimental point represented three Izod samples tested on the Wiedemann-Baldwin Impact Tester (#BL-1-1034). Impact energy information was organized according to processing and orientation for comparison in Izod energy versus rolling reduction plots.

2.7 Experimental Procedure: Cold Rolling and Annealing of PC Sheets and Samples

2.7.1 Cold Rolling

All of the rolled PC sheets and samples were processed through a two high Stanat Model F.100, 3 in x 5 in rolling mill. Maximum roll gap was approximately 0.31 in, roll diameter was 3 in, and roll width was 5 in. These dimensions effectively limited the unrolled material thickness to a nominal 1/4 in wheet which in most cases ranged from 0.240-0.248 in.

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*Per conversations with Mr. H. H. Bierenfeld, Section Chief, Model Shop Cable and Wire PECC, Western Electric, Atlanta Works.

Basically, two types of cold rolling were performed--uniform and non-uniform as defined by the Δ parameter. (See Appendix 3 for a full explanation of Δ.) The uniform rolling involved reductions where $\Delta<1$ and this, in turn, meant a first pass thickness change of about 0.040 to 0.045 inch in the 0.245 in sheet. Non-uniform rolling meant much higher Δ values (in the range of 4 to 5) and multiple rolling passes to gradually reduce the thickness. For the tensile tests, sheet samples were uniformly reduced so that $r = 0.18$ and 0.30 (from equation 4). In addition a group of tensile samples 3/16 in thick were reduced uniformly from $r = 0$ up to $4 = 0.48$ in 4 steps. For the Izod tests PC was rolled to $r = 0.18$, 0.30, 0.40 and 0.48 uniformly; and to $r = 0.025$, 0.06, 0.18 and 0.30 non-uniformly. In the uniform case $\Delta<1$ while the non-uniform rolling had a range of values $4.2\leq\Delta\leq5.3$. All cold rolling was conducted dry and unlubricated to avoid stress cracking. An example of solvent induced stress cracking in the PC was noted during rolling. Some identification information had been recorded on one surface with a felt tip marker. After several rolling passes the PC under the black marking showed cracks and crazes while adjacent unmarked material did not. No other visible cracking or crazing took place during normal rolling. An interesting rolling failure mode is discussed in Appendix 6.

Possible structural changes caused by rolling were examined by Gel Permeation Chromatography (see Section 2.8).

Material temperatures during cold rolling were not measured but probably never exceeded a comfortably warm state when the rolled PC was pressed to the experimenter's cheek. An estimate of maximum surface temperatures is 110-120F (43-49C).

2.7.2 Annealing

Annealed tensile specimens in their finished form both notched and uniaxial were heat treated in a forced air oven prior to testing. Izod impact specimens were also annealed in the notched and unnotched condition. The annealing procedure was similar to that of Morgan and O'Neal [16] who found that "...In series B (compression molded PC tensiles 180C, 15 min, cooled 2 C/min to room temp), the yield stress attained following 3 hr annealing at 145C remained unchanged after 4 days further annealing at this temperature...." The authors indicated that this constant yield stress implies that the glass essentially attained an equilibrium state within three hours annealing at 145C. The annealed Izod samples were quenched in ice water by Morgan and O'Neal, but in the current work the different sets of annealed test pieces were quenched in tap water at about 55F (13C) and ice water 32F (0C).

Early efforts to anneal as-extruded tensile and Izod specimens revealed an unchanging characteristic of the machined test pieces. The residual stresses always relieved themselves unevenly no matter how carefully uniform heating was attempted by hanging them inside the oven. Every sample arced or essed to a degree that made it unusable. To overcome this problem, heavy metal plates were used to keep all samples under modest compression. Besides the straightening effect, the heat capacity of the plates provided perhaps a little more thermal stability than was provided by the forced air oven temperature control system. The 15 x 18 x 19 inch blue M ESP-400 BC-4 life test oven was controlled by a solid state proportioning temperature controller. The operating instructions claimed ±0.2C as a control tolerance while experiment showed that the 64 cubic inch volume in the center of the floor of the oven varied less than 0.1C. It was in this volume at 145C ± 0.1C that all annealing took place. Dimensions were carefully noted before and after the four hour anneal cycle at 145C. The extra hour was provided to allow the samples, preheated oven, and plates to come into equilibrium. In the tensile specimen case, samples were handled in the same manner as as-extruded or cold rolled from this point. The impact samples were of two groups; those notched before and those notched after annealing. From there the two groups of annealed samples were tested the same as the as-extruded and cold rolled PC.

2.8 Experimental Procedure: Gel Permeation Chromatography and Melt Flow Plastometry on the As-Extruded and Cold Rolled PC

2.8.1 Gel Permeation Chromatography

In order to determine the effects of cold rolling on the molecular structure of PC two types of tests were run on the as-extruded and uniformly rolled samples:

1. Melt flow tests (see 2.8.2)
2. Liquid chromatography

The melt flow test is a traditional test that is supposed to detect gross changes or differences in molecular weights or viscosities of polymer samples. Gel Permeation Liquid Chromatography has recently been developed into a high speed process (i.e. chromatograms produced in minutes). Coupled with data handling and computer techniques, this procedure can produce weight average and number average molecular weights plus dispersities almost as quickly as the chromatograms are produced.

The sensitivity of the chromatograph allowed separation of molecular weight components from 100 to 10,000,000. Compared to the melt flow tests GPC is very sensitive. Gel Permeation Chromatography is essentially a mechanical sorting of molecules based on their relative size in solution. This separation is accomplished by forcing the sample solution through a porous packing gel which is compatible with the mobile solvent. In this model tetrahydrofuran was the solvent used in the GPC columns. The smallest components of the PC sample migrate into the smallest pores of the gel while the size of the higher molecular weight fractions prevent them from penetrating as far into the packing material. Since the smaller molecules proceed through the columns by a more circuitous route, they are separated from the larger ones by the time the exit tube is reached. This separation is diagrammed in Figure 11.

In GPC there is no affinity of the sample for the packing gel. Therefore, the maximum amount of solvent required for complete sample elution will be equal to the column volume. This means that, effectively, all sample components elute within one column volume. As separated sample components elute from the column, they pass through one or more closely spaced detectors. By detecting the amount of UV absorbed and noting the refractive index of the elution vs volume or time, the detectors allow determination of the molecular weight fractions [17].

Samples of the as-extruded, $r = 0.18$, $r = 0.32$, and $r = 0.48$ PC were dissolved in a solution in tetrahydrofuran and injected into the Waters 440 GPC schematically represented in Figure 12. The resultant chromatograms were then processed to give both weight average and number average molecular weights.

2.8.2 Melt Flow Plastometry

In order to characterize the effects of uniform cold

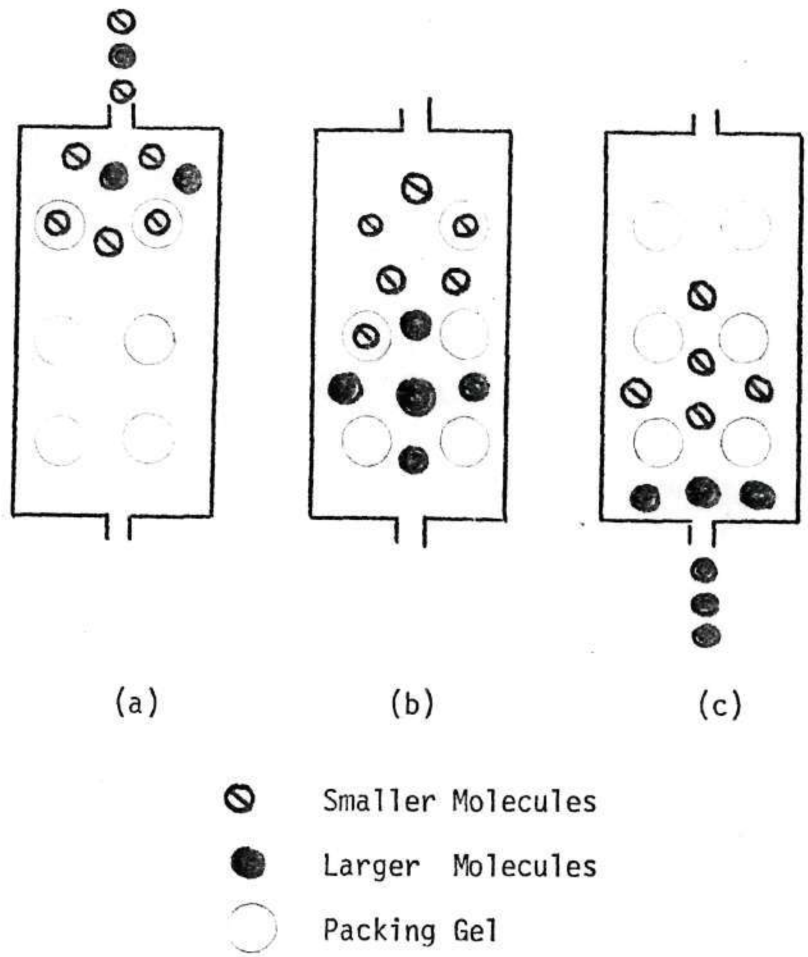


Figure 11. Schematic Separation of Molecular Weight Fractions During Gel Permeation Chromatography

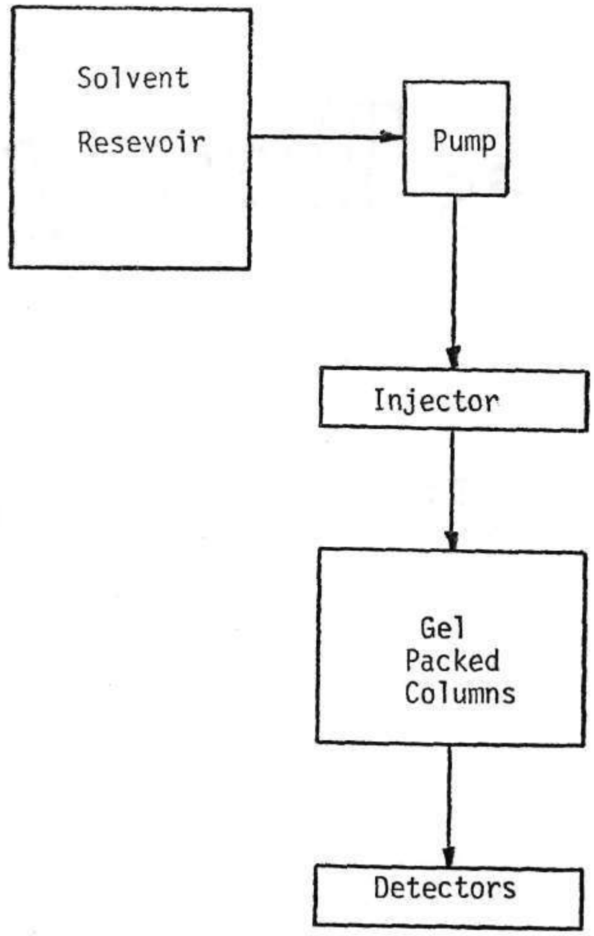


Figure 12. Gel Permeation Chromatograph - Function - Block Diagram

rolling on the molecular structure of PC, a traditional test used on pllymers was employed. Melt flow tests were run per ASTM D1238-73 [21] on samples of as-extruded, 1 pass ($r \approx 0.18$), and 2 pass ($r \approx 0.32$) PC. The plastometer charges were chipped off the three sample sheets, carefully mechanically diced, and thoroughly dried on a sample dish in a sample drying oven. The Tinius Olsen Thermodyne Plastometer was carefully cleaned with gun barrel patches and new brass wire brushes before the first run and between each of the other two runs.

The charge of diced, dried PC was loaded into the plastometer, and the tests were run at 300°C per ASTM condition "0" resulting in melt flow values in grams per 10 minutes. Figure 13 shows a schematic of the melt flow test apparatus and the principles of operation. The melt flow was determined by catching and weighing the extrudate from the plastometer during one minute of the time when the piston was traversing the ringed section at the barrel entry. This weight and time was converted into gtams/10 minutes. The particular orifice and piston weight was specified in condition "0" of the ASTM test.

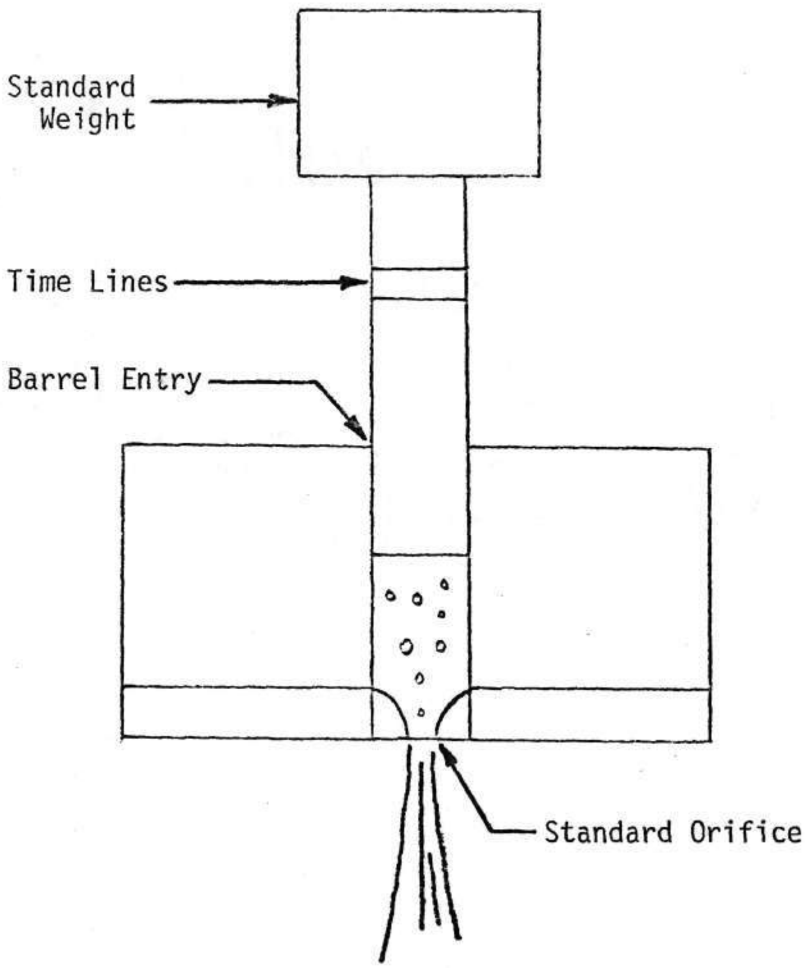


Fig. 13: Melt Flow Plastometer Schematic

CHAPTER III

RESULTS AND DISCUSSION OF RESULTS

3.1 Results

The experimental stress-strain data for the originally 1/4 in as-extruded, annealed, and cold rolled uniaxial PC specimens is displayed in Table 1 for the 0.5%, 1.0%, 2.5% offset stresses, and maximum load offset point before load drop. In a similar manner, Table 2 displays this information for the as-extruded notched tensile specimens where $\theta = 90°$, $75°$, $55°$, and $30°$. Dimensions on these specimens follow Figure 5. The annealed notched tensile data is shown in Table 3 for $\theta = 90°$ and $45°$. Since these specimens followed the dimensions of Figure 6a, the as-extruded notched data from this same design is included in Table 3 for $\theta = 90°$ and $45°$.

Data from the uniformly cold rolled notched tensile samples is shown in Table 2 for $\theta = 90°$ at the several degrees of rolling reduction r from equation (4). Additional information on as-extruded and cold rolled uniaxial tensile specimens is displayed in Figure 14 where the yield stress is plotted against equation (4) for the 0.5%, 1.0% and 2.5% offset stress values. Figure 14 was derived from data for 3/16 in tensile samples that were cold rolled to various

Table 1. Uniaxial Yield Strength at Various Strain Offsets--As-Extruded, Cold Rolled, and Annealed PC

	psi[3]			Max.[2]	
Rolling Reduction[1]	0.5%	1.0%	2.5%	Load	Comment
r = 0	8450	9250	--	9375	X1,as extruded
r = 0.18	7560	--	--	7690	X1,one pass
r = 0.30	8025	8250	--	8330	X1,two pass
r = 0	7250	8440	9570	9600	X2,as extruded
r = 0.18	6880	7160	6900	7160	X2,one pass
r = 0.30	6550	6975	6850	7050	X2,two pass

[1] All samples both as-extruded and cold rolled were "cored" so that every unaxial was approximately 0.070" thick

[2] Max load offset yield strengths fall between 1 and 3 percent true strain.

[3] Average of three samples.

Table 2. Notched Tensile Yield Strength at Various Strain Offsets (Hill's Constraints)--As-Extruded and Cold Rolled PC

	psi				
θ	0.5%	1.0%	2.5%	Max. Load	Comment
90°	8800	9400	10150	10150	X1
75°	7500	8200	8850	9330	X1
55°	6700	7100	8150	9250	X1
30°	--	--	6150	11970	X1
90°	8300	8500	8860	11600[1]	X1,r=0.18
90°	6470	7320	8770	-2-	X1,r=0.30

[1]Offset here was approximately 50%.

[2]No maximum load occurred as the samples failed while the load was still increasing.

Table 3. Notched Tensile and Uniaxial Yield Stresses at Various Strain Offsets (Lee Constraints)--As Extruded and Annealed PC

Notched θ	psi 0.5%	1.0%	2.5%	Max Load	Comments
90°	6740	8300	10350	10450	X1,as-extruded
45°	6630	8600	10200	9800	X1,as-extruded
90°	7980	9500	11400	(brittle failures)	X1,annealed
45°	5760	7800	11450	11800	X1,annealed
Uniaxial					
r=0	7660	8750	9000	9150	X1,as-extruded
r=0	6560	7720	9100	9100	X1,annealed

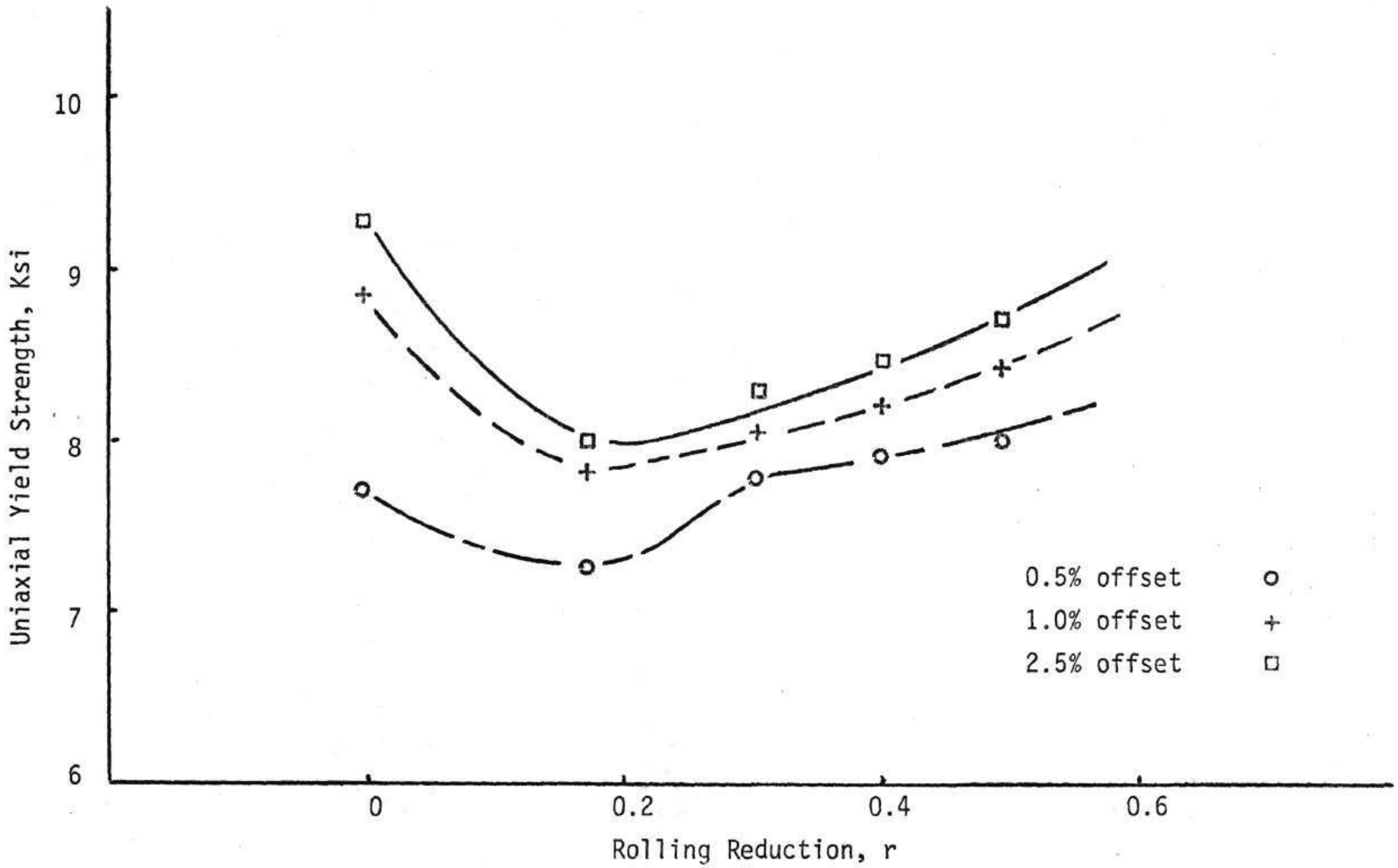


Figure 14. Uniaxial Yield Strength versus Rolling Reduction,r for Various Strain Offsets, h_0= 3/16 inch PC

degrees ($r = 0.18$ to $r = 0.48$). Figure 15 shows this same information from the 1/4 in PC sheet that was cold rolled first and then where "cored" uniaxial tensile specimens were produced in a manner described in Section 2.4.

Post yield values of transverse strain ratios R and P vs ε_t are plotted and linearly extrapolated through $\varepsilon_t = 0$ for $r = 0$, 0.18, and 0.30 in Figures 16 through 21. The results of the plane strain compression tests on as-extruded and cold rolled PC are shown in Table 4. Izod impact results are represented in Figures 22 through 25 where impact energies are plotted against rolling reduction for the cold rolled PC for both the uniformly and non-uniformly rolled material. The as-extruded and annealed Izod energies are plotted versus thickness. In all cases the notch tip radius (NR) on the Izod samples is indicated.

Molecular structure information in the form of weight average and number average molecular weights versus rolling reduction plus melt flow values is shown in Figure 26 and Table 5.

3.2 Discussion of Results: Uniaxial Tension Tests of As-Extruded, Annealed, and Cold Rolled Polycarbonate (PC)

Table 1, the as-extruded ($r=0$) uniaxial tensile data, indicates planar anisotropy at the 0.5% and 1.0% strain offset stress levels. However, the 2.5% and maximum load

Table 4. Compressive Yield Strengths at Various Strain Offsets for Cold Rolled PC

		ε			σ
Condition	Thikns	0.5%	1.0%	2.5%	Max
As-Ext	0.240	10,600	11,200	12,200	13,200
r = 0.18	0.200	8,000	8,700	10,000	12,800
r = 0.27	0.175	9,000	10,300	11,900	12,600
r = 0.38	0.150	9,200	10,600	11,900	14,000
r = 0.42	0.140	8,900	9,800	10,500	12,800

Table 5. Chromatography and Melt Flow Data for PC at Various Rolling Reductions, r

r	$\bar{A}_n$	$\bar{A}_w$	Melt Flow g/10 min
0	12,100	29,500	8.8
0.18	10,900	29,200	8.6
0.30	11,100	28,600	8.7
0.48	10,800	28,800	--

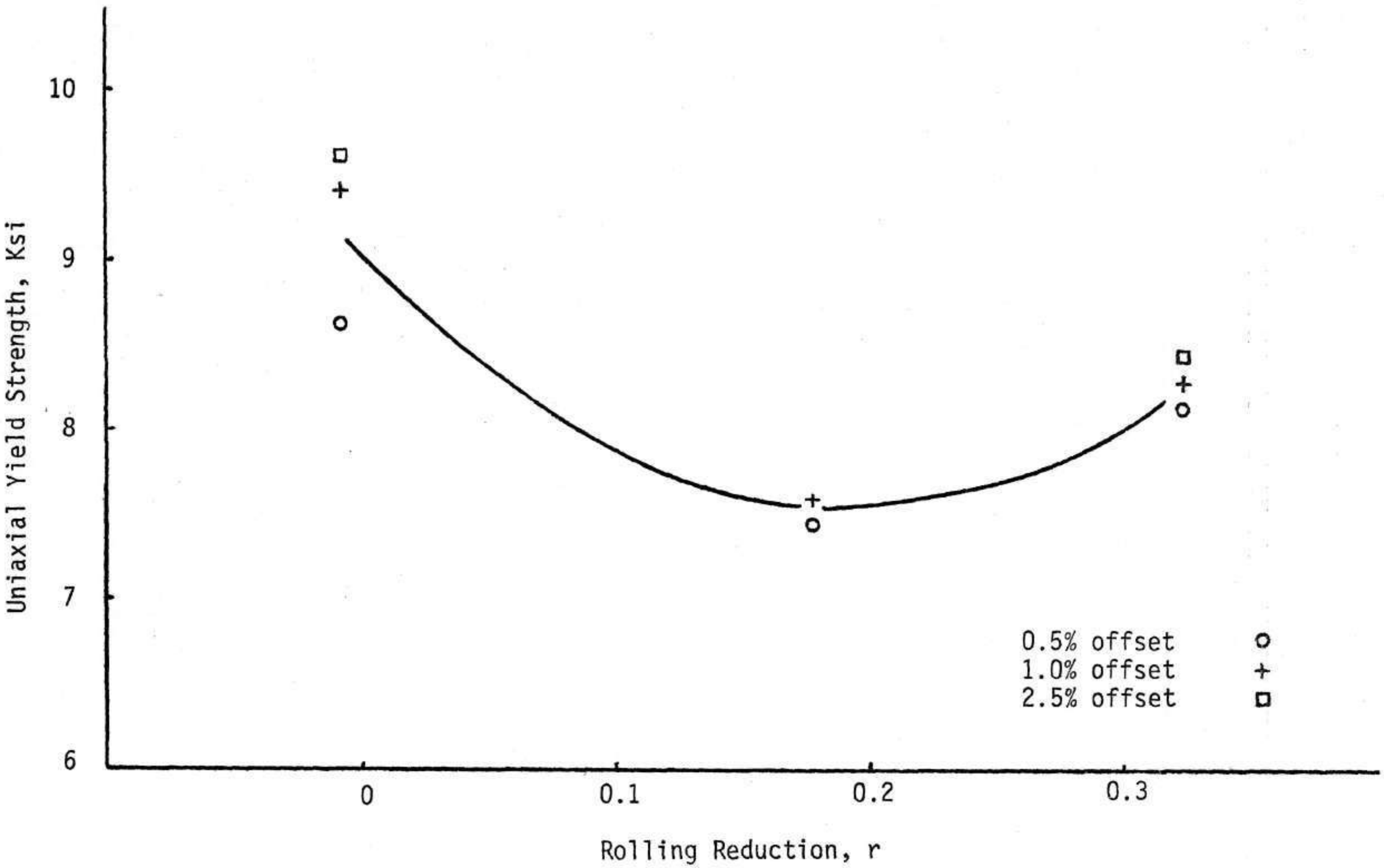


Figure 15. Uniaxial Yield Strength versus Rolling Reduction, r for Various Strain Offsets - h_0 = 1/4 inch PC

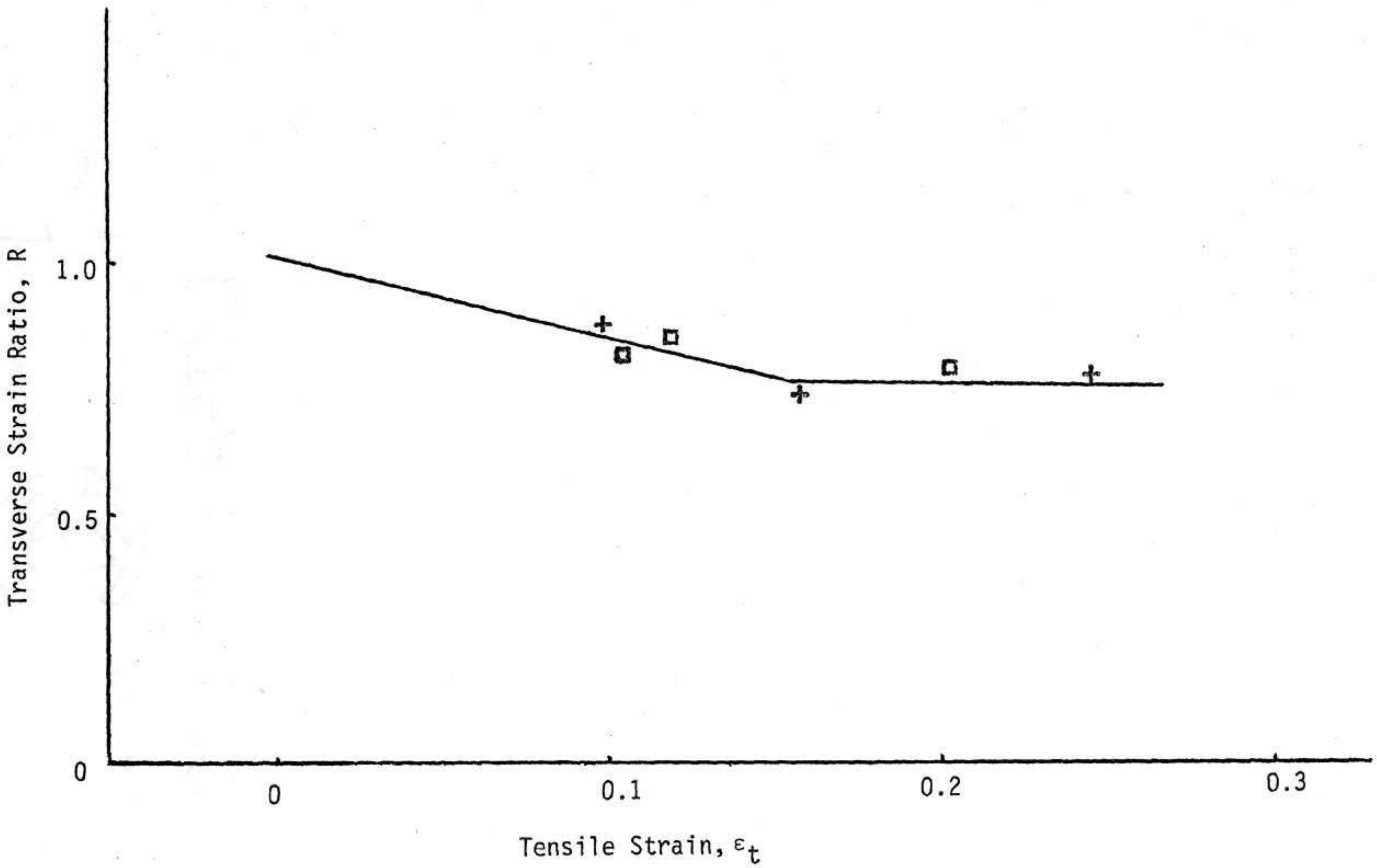


Figure 16. Transverse Strain Ratio, R versus Uniaxial Tensile Strain ε_t - As-Extruded PC

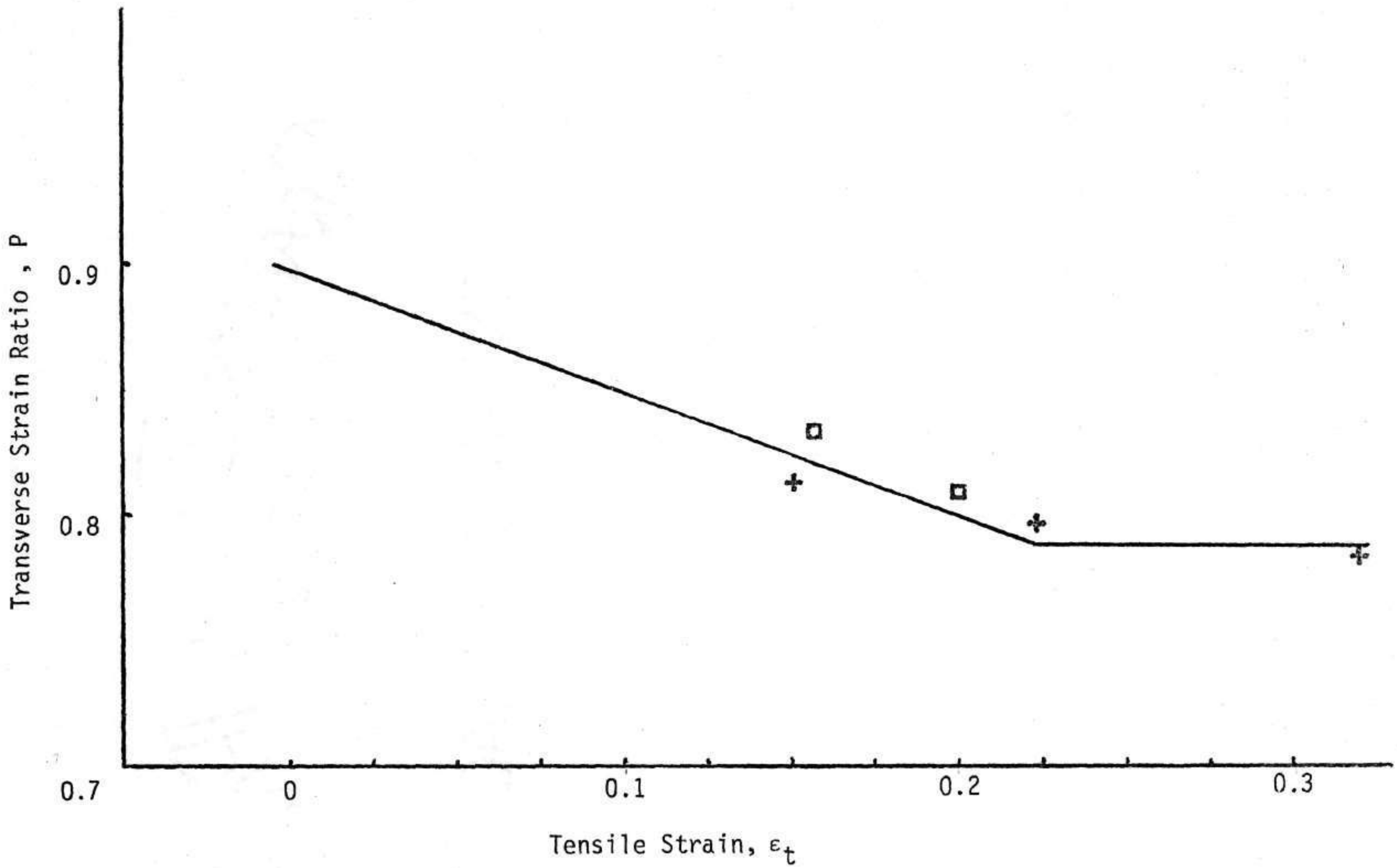


Figure 17. Transverse Strain Ratio, P versus Uniaxial Tensile Strain ε_t As-Extruded PC

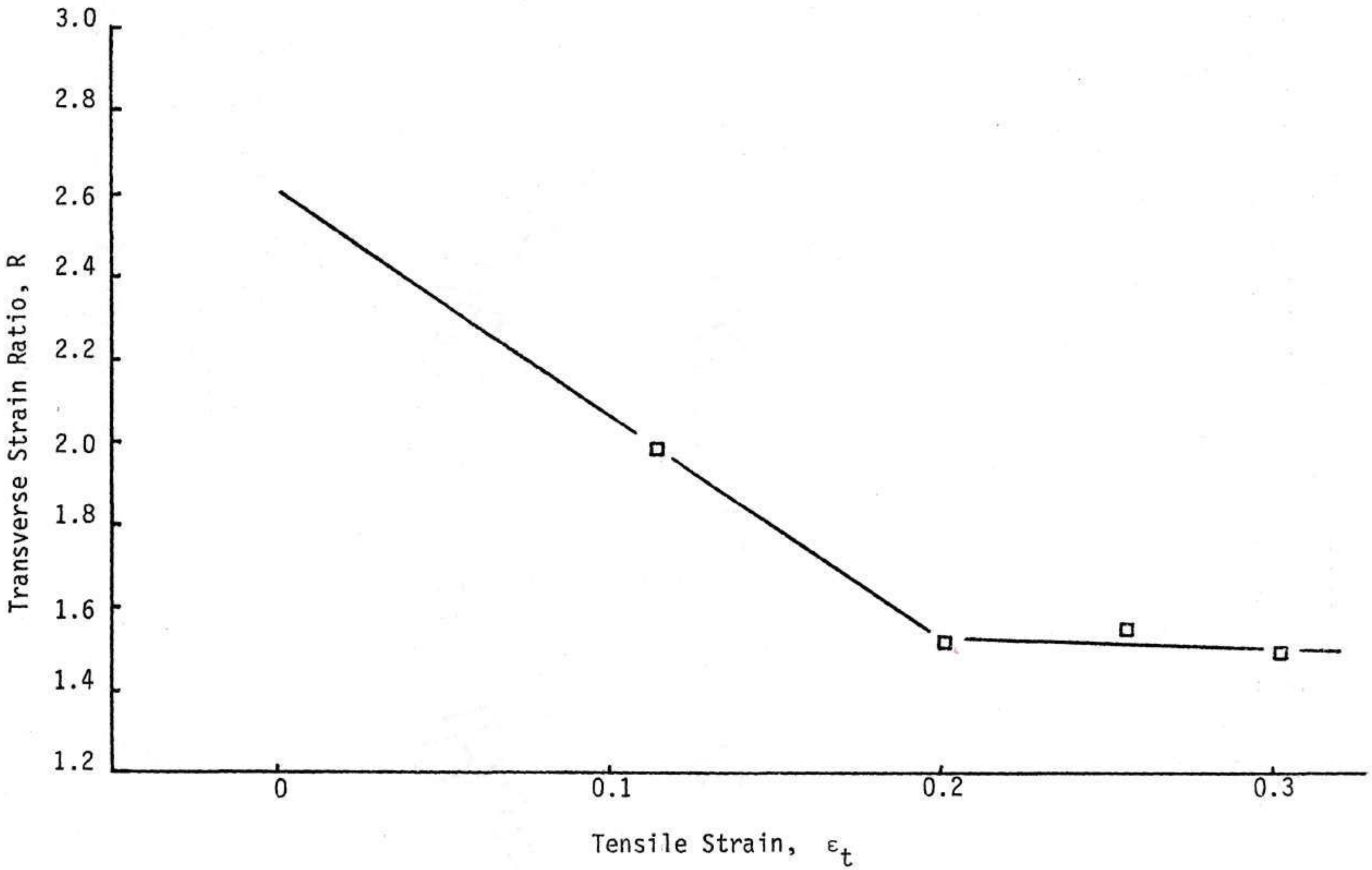


Figure 18. Transverse Strain Ratio, R versus Uniaxial Tensile Strain ε_t- Cold Rolled PC, r = 0.18

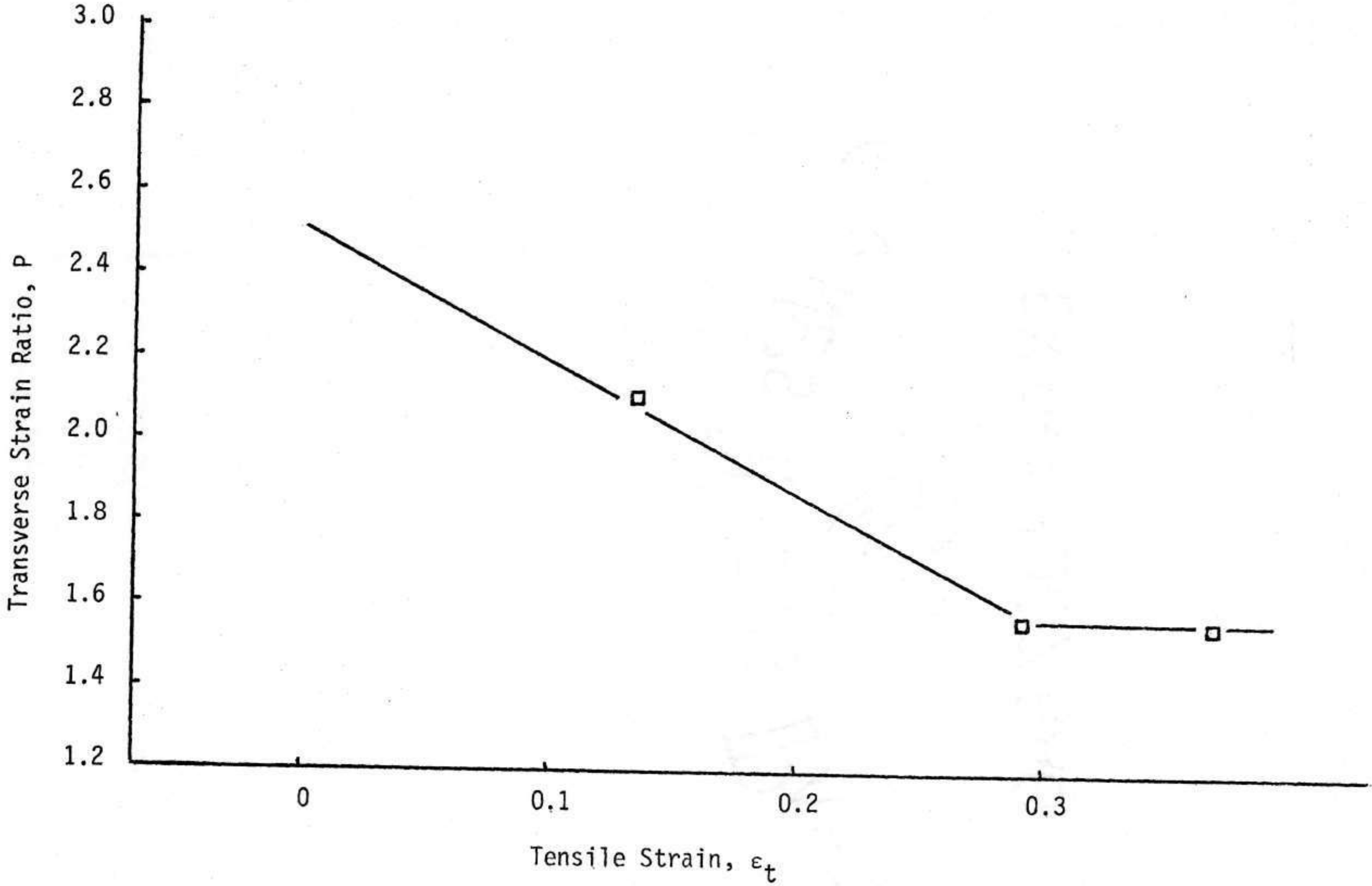


Figure 19. Transverse Strain Ratio, P versus Uniaxial Tensile Strain, ε_t - Cold Rolled PC, r = 0.18

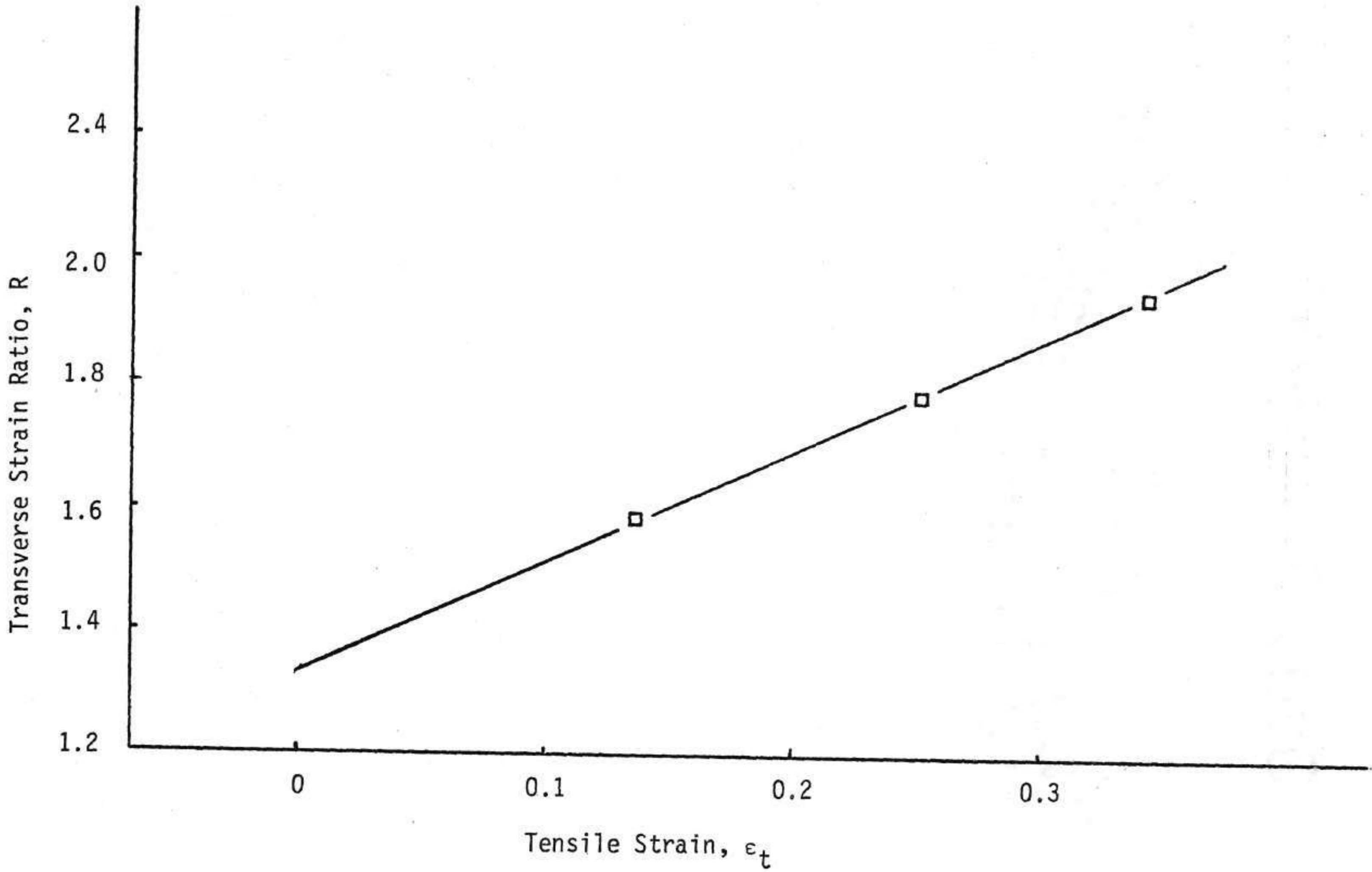


Figure 20. Transverse Strain Ratio, R versus Uniaxial Tensile Strain ε_t - Cold Rolled PC, r = 0.30

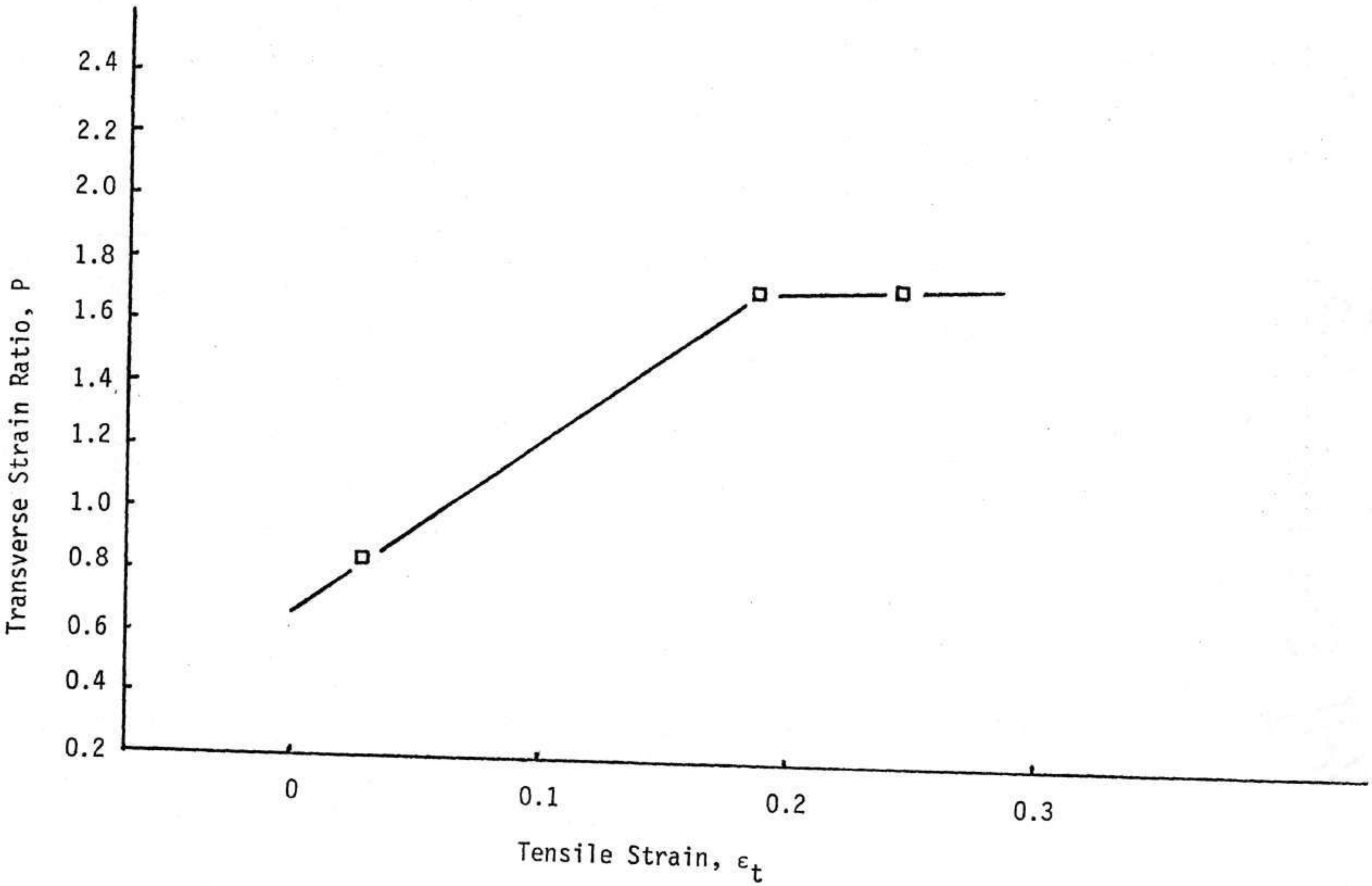


Figure 21. Transverse Strain Ratio, P versus Uniaxial Tensile Strain ε_t - Cold Rolled PC, r = 0.30

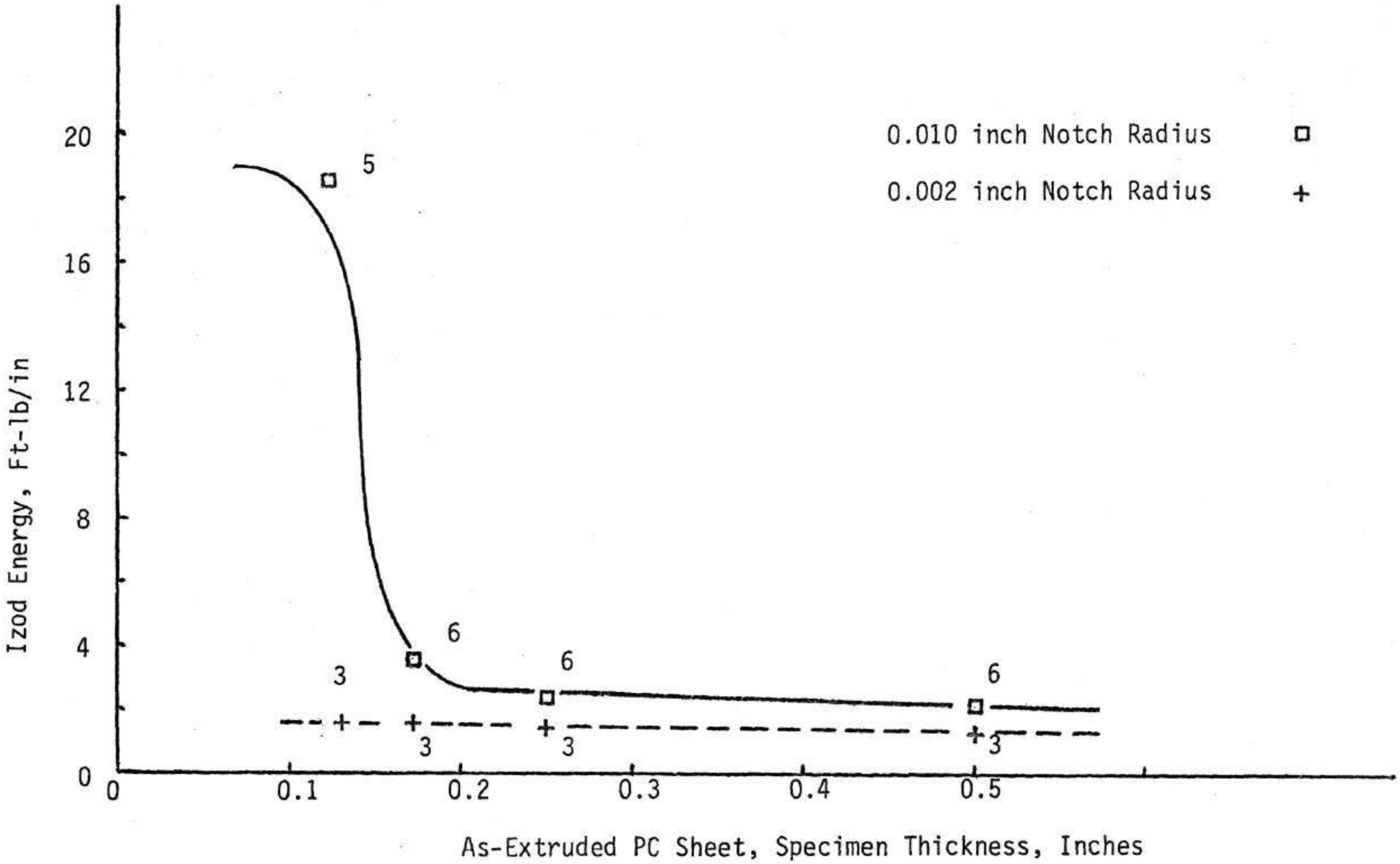


Figure 22. Izod Energy versus Sheet Thickness, As-Extruded PC

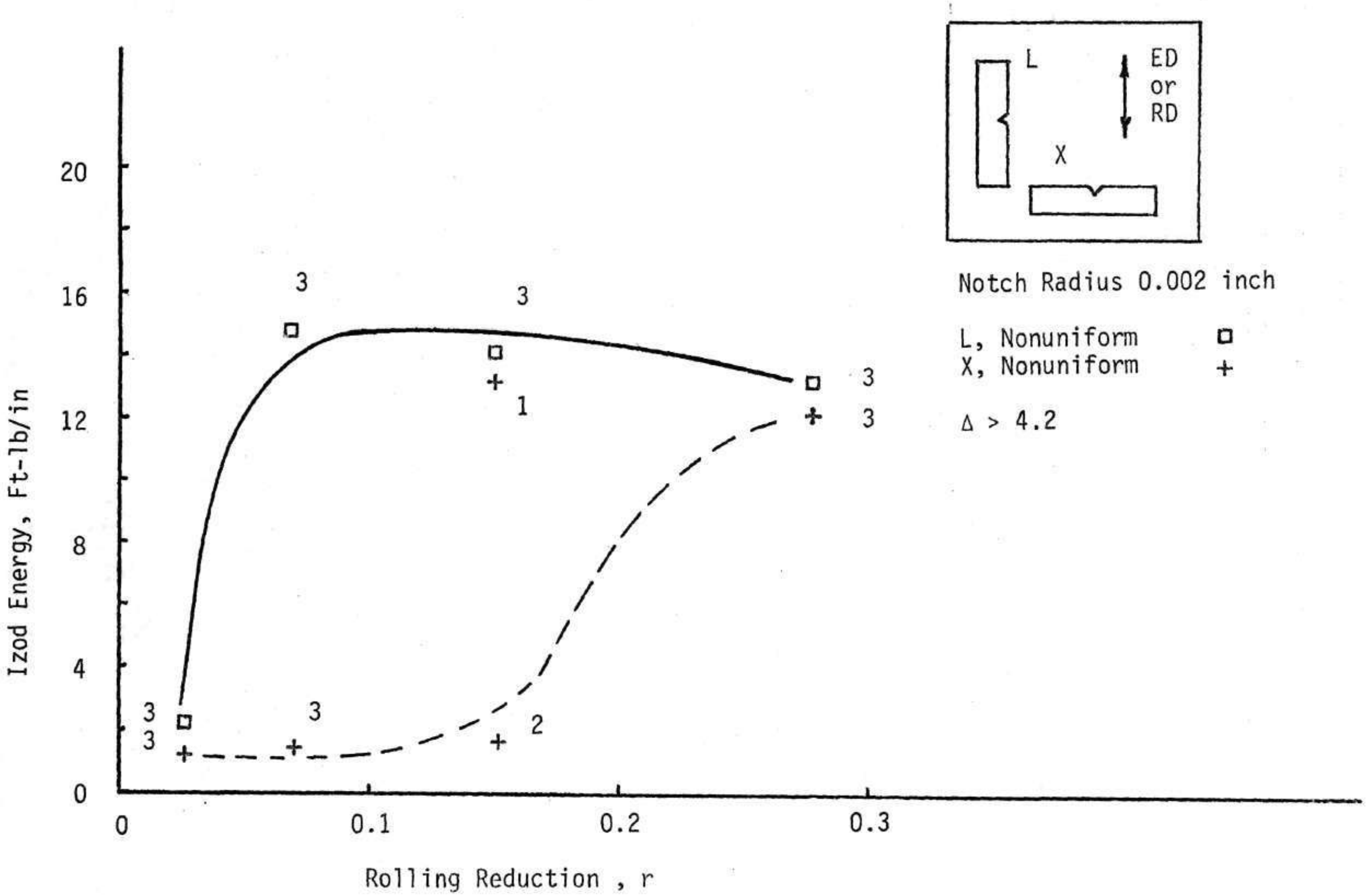


Figure 23. Izod Energy versus Nonuniform Rolling Reduction
$h_0 = 0.25$ inch

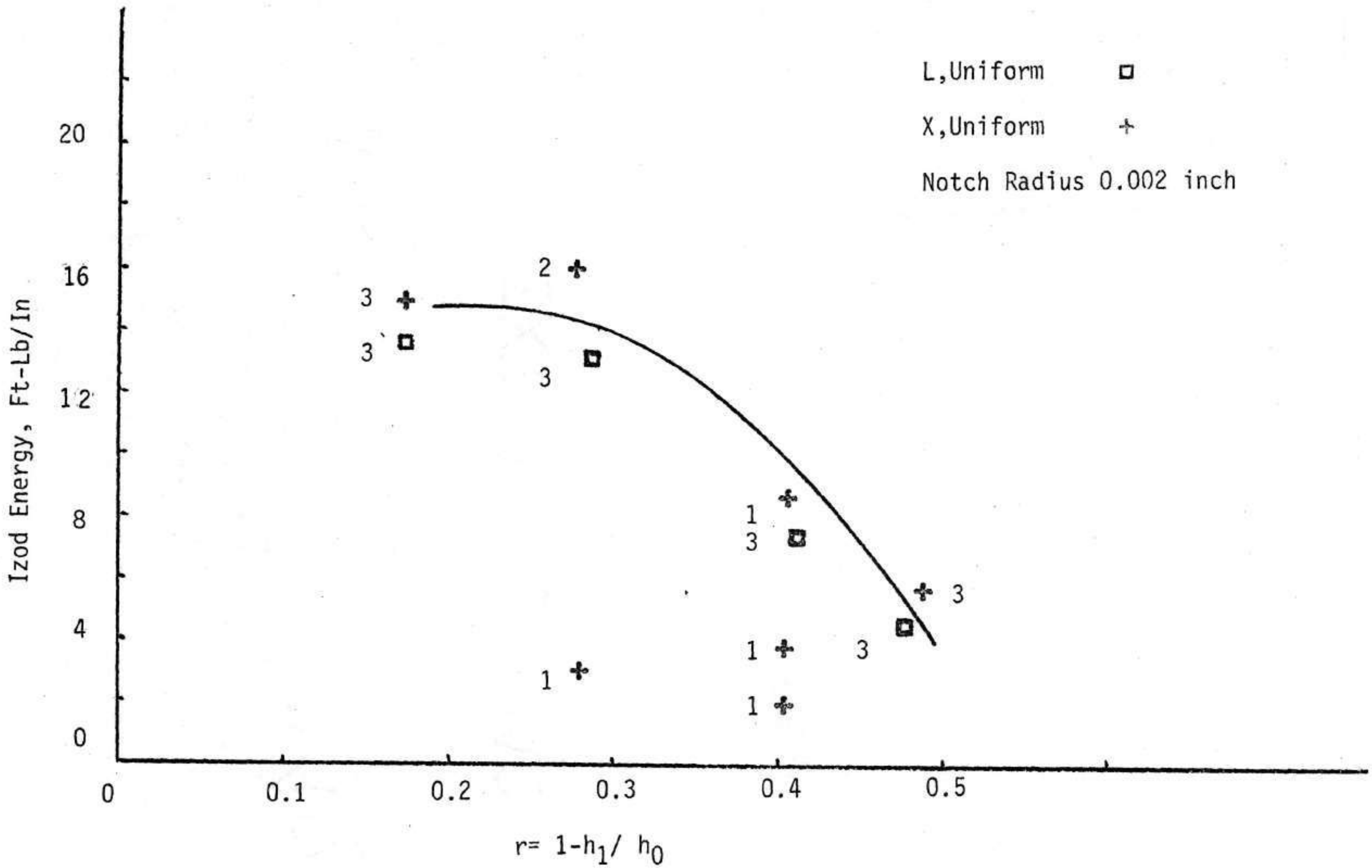


Figure 24. Izod Energy versus Uniform Rolling Reduction, r
h_0 = 0.25 inch

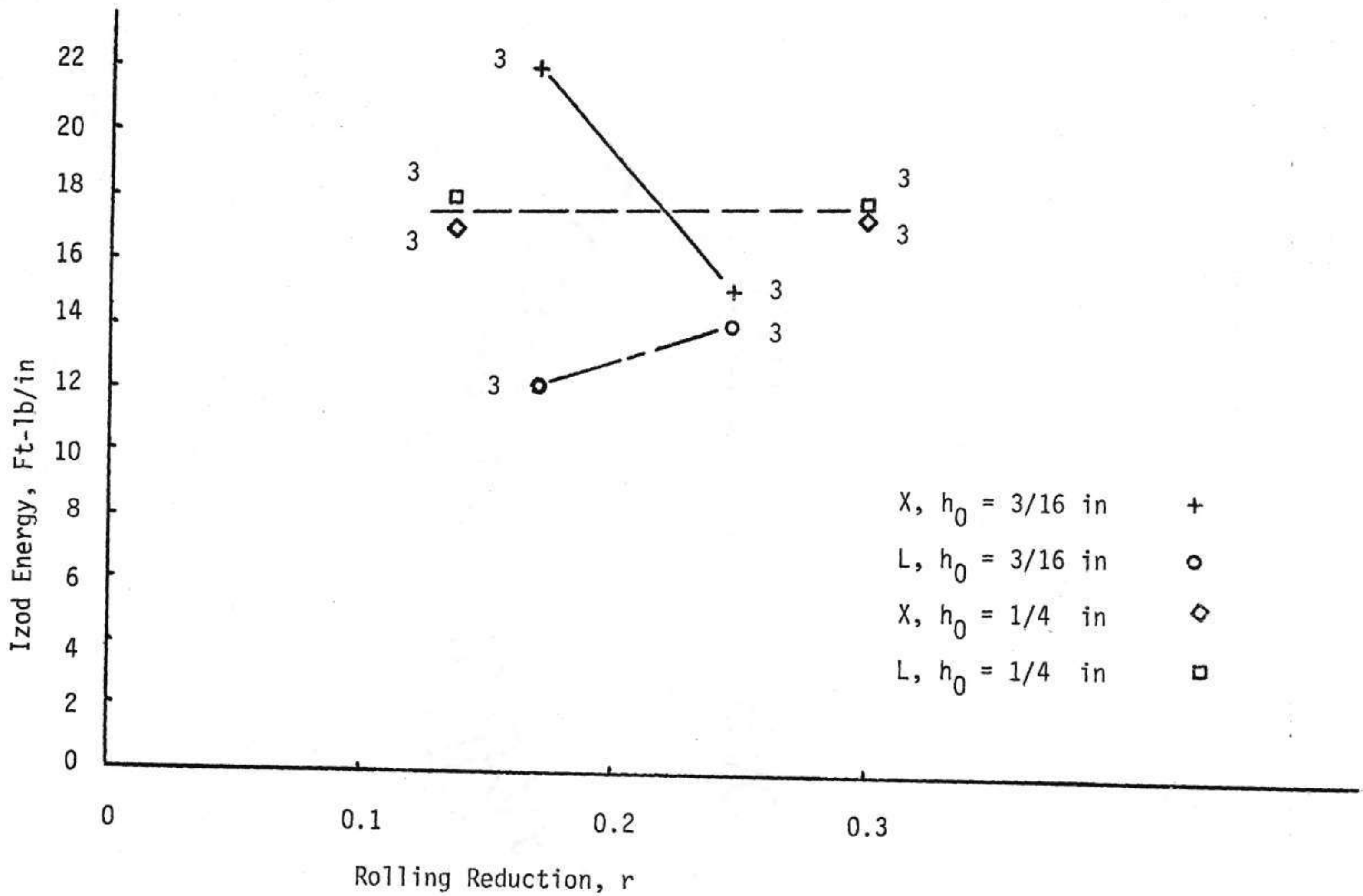


Figure 25. Izod Energy versus Uniform Rolling Reduction, r
Notch Radius = 0.010 inch , h_0 = 3/16 and 1/4 inch

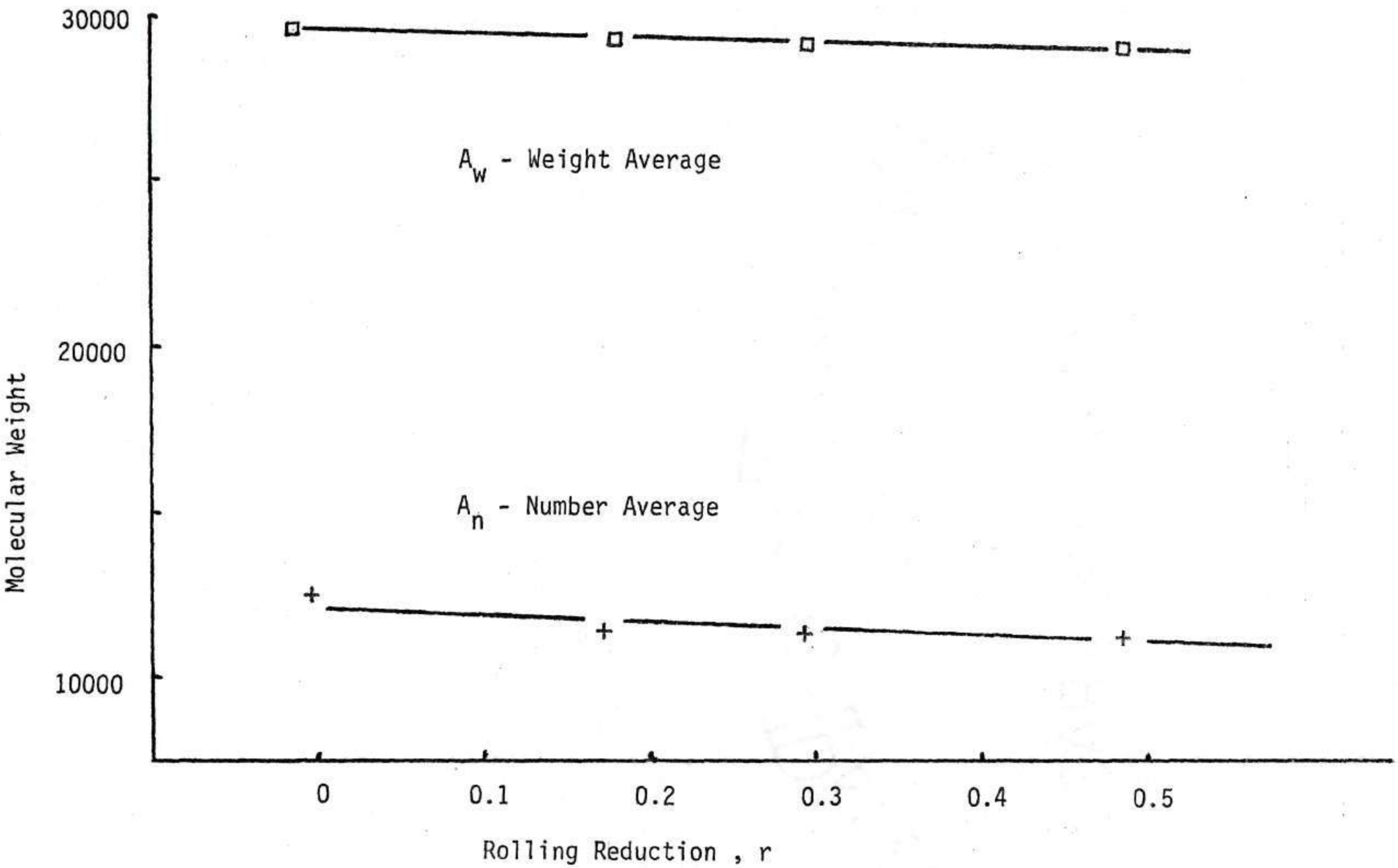


Figure 26. Weight Average and Number Average Molecular Weight versus Uniform Rolling Reduction ,r - h_0= 0.25 in

offset values are about the same in the X1 and X2 directions. This might be explained by some molecular orientation during the sheet extrusion process in the X1 direction that manifests itself at the low permanent strain levels. Comparing the X1 and X2 directions in Table 1 at $r = 0.18$ which corresponds to one pass uniform cold rolled PC, reveals a 6 to 10 percent higher yield stress level in the X1 direction throughout the strain offset range examined. Similarly, when $r = 0.30$ (two pass uniform cold roll), the X1 direction shows an 18 to 22 percent higher yield strength level at the four offsets recorded.

It is also interesting to note that in both cold rolled cases and directions that the yield strength arrives at the 0.5% point within about 4 to 7% of the maximum load offset value while the as-extruded values climb 11% and 32% in the X1 and X2 directions, respectively. Indeed, the whole pattern of the uniaxial sample behavior as expressed in the matrix of Table 1 is:

(1) In the X1 direction, cold rolling at first depresses the yield strength ($r = 0.18$) but further rolling ($r = 0.30$) starts to raise the yield strength toward the as-extruded values. The literature [6,7] confirms this observation. In fact, further rolling maximizes the X1 yield strength at a level greater than the $r=0$ value.

(2) The X2 direction yield strength is similarly

depressed at r = 0.18 but does not recover any at the next level of uniform rolling reduction (r = 0.30). The effects of further rolling on X2 have not been detailed in the literature examined.

A summary of the information in Table 1 concerning the as-extruded and cold rolled uniaxial tensile isotropy is as follows:

(1) The as-extruded PC appears planar isotropic in nature.

(2) After the first uniform cold rolling pass, there is some measurable anisotropy since X1 yield strength values range 6 to 10 percent higher than X2. Even after allowing for experimental error (which should be less than 3 to 5%) a significant difference remains. Overall this state could be broadly classified as planar isotropic (X1-X2).

(3) After the second uniform rolling pass (r = 0.30), the data indicates clearly that planar anisotropy exists, as the X1 values are approximately 20% greater than the X2 direction.

The annealed uniaxial data shown in Table 1 indicates a depression in the 0.5% and 1.0% offset values relative to the as-extruded case while the 2.5% point (and/or maximum load offset) is within a few percent (i.e. experimental error) of the X1 as-extruded values. One possible explanation is that the extrusion orientation postulated in the X1 direction is relieved by heat treatment. Several sources demonstrate that annealing near T_g will restore physical and thermodynamic equilibrium to glassy polymers and PC in particular [4,5,16].

Examination of the uniaxial yielding process after the maximum load is very important in obtaining post yield values of the transverse strain ratios R and P. In the transient period between load drop and cold drawing in as-extruded PC, the changes in width and thickness described the changing values of P and R as they approached the cold drawing values. In the r = 0.18 material and r = 0.30 cold drawing values of P and R are approached, but at higher strain levels.

By extrapolating the values obtained during the transition, a value at $\varepsilon_t = 0$ is produced for P and R at r = 0, 0.18, and 0.30 which provides an approximate measure of the relative isotropy present initially in the sheet PC and the degree of anisotropy produced by cold rolling. Figures 16 through 21, demonstrate graphically the qualitative and quantitative differences at the several levels of rolling defomration. In the as-extruded samples, cold drawing appears well established by at least $\varepsilon_t = 0.25$ for both P and R. Figures 16 and 17 should ideally yield R = P = 1.0 for planar isotropic material. This is only approximately true for the extrapolated data. Both parameters P and R indicate strain softening up to the cold drawing process at constant values of approximately 0.8 for both.

The one pass cold rolled PC ($r = 0.18$) Figures 18 and 19 behaves in a similar manner in P and R versus ε_t. Both parameters extrapolate in the neighborhood of 2.5 at $\varepsilon = 0$ and both exhibit strain softening with increasing strain similar to the as-extruded PC. The next uniform rolling pass ($r = 0.30$) produces a change in both the level and kind of P and R values produced. Figures 20 and 21 show extrapolations of $P \simeq 0.6$ and $R \simeq 1.3$ at $\varepsilon_t = 0$. Furthermore, the uniaxial specimens are now strain hardening with respect to P and R. Cold drawing was reached in P vs ε_t but not in R vs ε_t. Perhaps data taken at greater strains would provide cold drawing.

As noted in Section 2.4, a neck formed coincident with the maximum load in the as-extruded unaxial specimens while no necking occurred in the samples made from either case ($r = 0.18$ or 0.30) of cold rolled PC. Indeed, the whole gauge length appeared to reduce in thickness and width in a continuous fashion. Cold drawing in the as-extruded PC was indicated by the spreading of the neck throughout the gauge length. Although the data clearly indicate a state of cold drawing existing in some of the cold rolled PC samples, a corresponding visual indicator did not appear.

Additionally, cold drawing appeared at a much higher level of P and R values in the rolled material than the as-extruded PC. In the r = 0.18 case both P and R have been reduced from the 2.5 range to about 1.5 while in the r = 0.30 case the P value increases from 0.6 at $\varepsilon_t = 0$ up to about 1.9 and R moves from 1.3 to a range of 1.9 to 2.3.

Bahadur [23] reported cold drawing in PC and indicated that cold rolling reduced it in his work and also in earlier work by Broutman in 1969. Hill's yield criterion for a plastically anisotropic material combined with the associated flow rule produces expressions for the plastic counterparts of Hooke's Law for an anisotropic material. Using the expressions R and P in tension in terms of F, G and H in the anisotropic Levy-Mises equations plus the strain ratios leads to expressions of tensile yield stress ratios in terms of R and P (for a more complete treatment of this subject, see Appendix 4):

$$\frac{\sigma Y_3}{\sigma Y_1} = \sqrt{\frac{(1+R)P}{(R+P)}} \tag{6}$$

$$\frac{\sigma Y_3}{\sigma Y_2} = \sqrt{\frac{R(1+P)}{(R+P)}} \tag{7}$$

The current effort has produced yield strenghts in the X1 and X2 directions. The results from equations (6) and (7) can be combined to produce

$$\frac{\sigma Y(2)}{\sigma Y(1)} = \frac{\sigma Y(3)}{\sigma Y(1)} \times \frac{\sigma Y(2)}{\sigma Y(3)} \tag{8}$$

Simply stated, the reciprocal of the result of equation (7) is multiplied times the result of equation (6). The results of equation (8) compared to the actual experimental values for this yield strength ratio provide a measure of the compliance of PC with the plastic anisotropic yield theory. Table 6 shows how closely the predicted stress ratio of the transverse to the longitudinal follows the experimental values. Considering the simple linear extrapolations and approximations involved in determining P and R values this close correlation is significant. Tensile yield stress values in the X3 direction can be calculated using the calculated stress ratios from equations 6 and 7 plus the maximum load experimental values from σY_1 and σY_2 at the several degrees of rolling reduction. The resulting yield strength will fall in the range of calculated values shown in Table 7.

Figure 27 displays the average experimental values for the max load yield strength versus the rolling reduction for the X1 and X2 direction plus the calculated maximum load (mid range) yield strength versus r for the X3 direction. The conditions of relative isotropy can be inferred from Figure 27 in the following manner:

(1) The as-extruded sheet is essentially isotropic

Table 6. Predicted and Actual Yield Stress Ratios Versus Rolling Reduction, r

Rolling Reduction (r)	P	R	Predicted $\sigma Y(2)/\sigma Y(1)$	Actual* $\sigma Y(2)/\sigma Y(1)$
0	0.9	1.0	0.97	1.02
0.18	2.5	2.6	0.99	0.93
0.30	0.6	1.3	0.81	0.85

*Max load yield stresses from Table 1.

Table 7. Calculated X3 Yield Stress Ranges Versus Rolling Reduction, r

r	σY_3 (max load) psi
0	9100-9600
0.18	9600-10,200
0.30	7100-7300

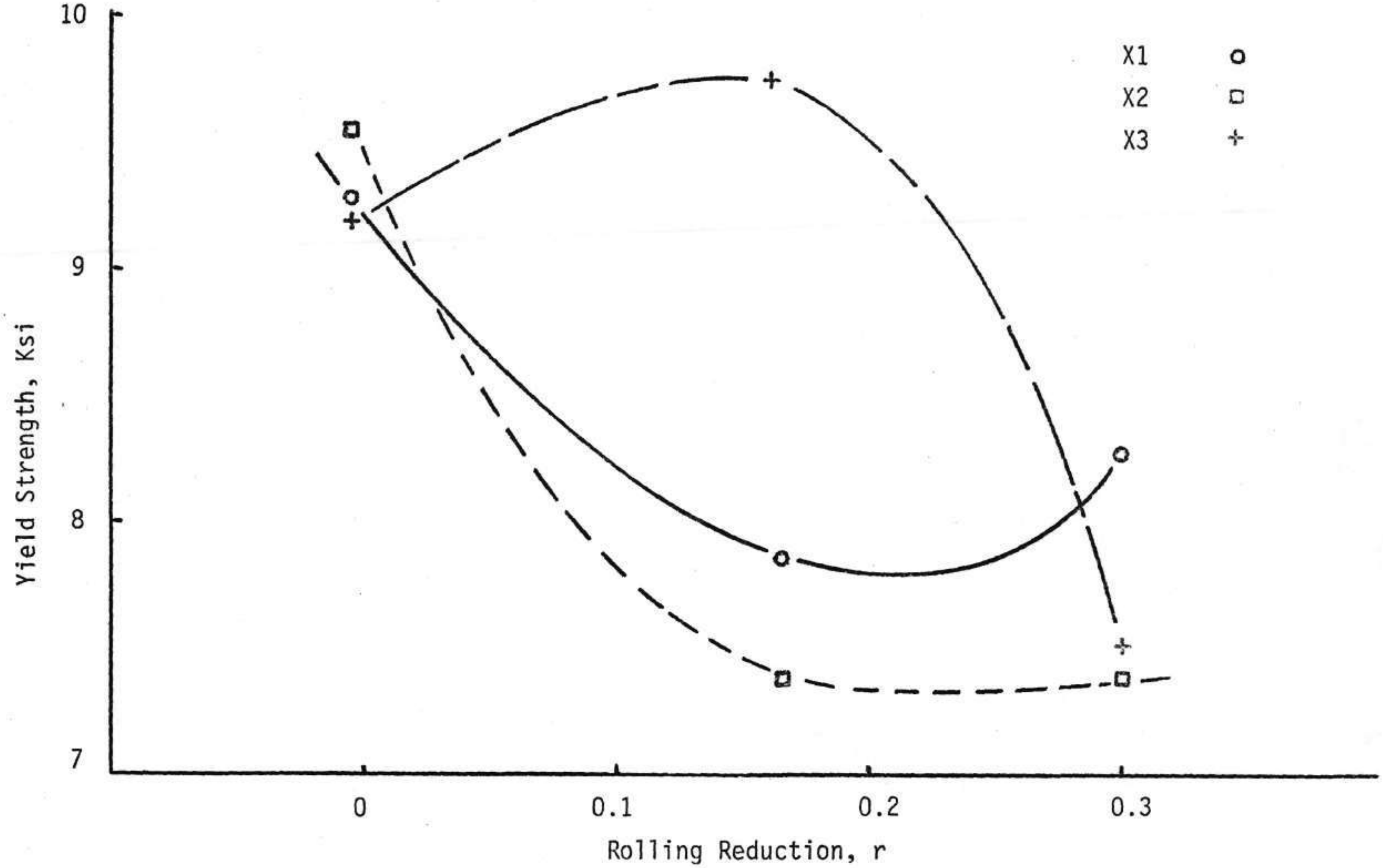


Figure 27. Uniaxial Yield Strength X1,X2,X3(Calculated) versus Uniform Rolling Reduction, r, $h_0 = \frac{1}{4}$ inch PC

in three dimensions.

(2) The single pass material ($r = 0.18$) is approximately planar isotropic (X1-X2) at reduced strength with about the original through-the-thickness strength (X3).

(3) The two pass material ($r = 0.30$) is again planar isotropic but the plane has shifted from X1-X2 at $r = 0.18$ to the X2-X3 plane at $r = 0.30$. The yield strength in the rolling direction (X1) has recovered nearly half of the loss incurred at $r = 0.18$ while the transverse planar yield (X2) remains approximately the same as its $r = 0.18$ value. The calculated yield in the X3 direction suggests the X2-X3 planar isotropy.

Another group of uniaxial samples examined for their tensile behavior were prepared in a slightly different fashion. After machining tensile specimens from 3/16 in (nom) PC sheet, the tensile specimens were cold rolled uniformly ($\Delta<1$) from $r = 0$ to $r = 0.48$ in the X1 direction. Figure 14 displays the yield stress as a function of rolling reduction r at the three offsets (0.5%, 1.0%, and 2.5%). The maximum load stress values for these samples were nearly coincident with the 2.5% offset points. A similar plot is shown in Figure 15 for the X1 data from Table 1. This behavior was noted by Broutman and Patil [6] in their investigation of the influence of cold rolling on the properties of amorphous polymers. In both Figures 14 and 15, only the $\varepsilon_t = 0.005$ curve in Figure 14 shows an increase in yield stress beyond the $r = 0$ value. However, the trend of the curves is positive and indeed, at higher rolling reductions, Broutman reports yield strengths exceeding the as-extruded values. This observed trend of depression of yield strength at low rolling reduction followed by increased yield strengths can be explained in terms of two processes:

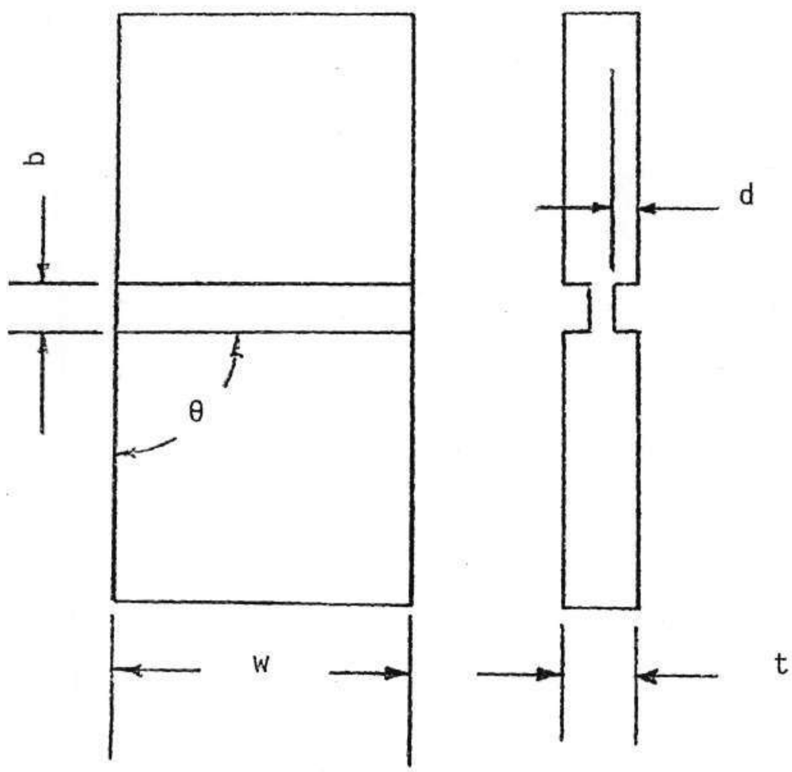
(1) Increase in free volume or decrease in supermolecular order. Legrand [33] suggested that a variety of events including annealing and prestraining would initially depress the yield strength of PC due to an increase in free volume. Based on a theoretical Maxwell element model, Legrand proceeded mathematically to the conclusion that a slight increase in free volume results in decreased yield strength. Broutman and Patil [6] and Bahadur and Henkin [7] argued from a physical viewpoint that the rolling resulted in a disrupting of the supermolecular order that was present resulting in lower yield stresses after light rolling.

(2) Increase in molecular orientation. Broutman and Patil [6] displayed birefringence data to suggest that at greater rolling reductions there is significant molecular orientation in PC in the rolling direction. This accounted for the improved yield strengths in the rolling direction.

3.3 Discussion of Results: Plane Stress-Plane Strain Notched Tensile Tests--As-Extruded, Annealed, and Cold Rolled Polycarbonate (PC)

Notched tensile specimens have received attention in the past primarily in metals work but also in polymer investigations. The wealth of constraints used in the past can be best detailed using Figure 28 and Table 8. Although Hill is probably one of the most notable figures in this whole area of deformation and plasticity, he has been, to a large degree, ignored in his recommendations on sample width relative to notch width (w/b). In his 1953 paper, Hill [8] stated, "In order to reduce edge effects to negligible proportions the width of the strip should be some twenty to thirty times the breadth of the groove, which in turn should be somewhat greater than the remaining thickness..." Four out of five other sources shown in Table 8 ignored this constraint. However, four out of five followed his other constraints.

The notched tensile data for as-extruded and cold rolled PC using Hill's constraints is shown in Table 2 while Table 3 shows similar information for Lee type constraints. The notch orientation angle varies from 30° to 90° covering portions of the fourth and first quadrants of the X1-X2 stress plane. In the Hill samples, the as-extruded group contained notch angles of 30°, 55°, 75°, and 90°. According to Nadai [19], a thin and wide uniaxial



w = specimen width, in.

t = plate or sheet thickness, in.

b = face notch width, in.

d = face notch depth, in.

θ = angle of notch inclination, degrees

Figure 28. Plane Strain Notched Tensile Specimen Dimension Terminology

Table 8. Plane Strain Notched Tensile Sample Dimensional Constraints from Earlier Investigations

Author	Ref.	$\frac{w}{b}$	$\frac{w}{t}$	$\frac{b}{t}$	$\frac{t}{d}$	t-2d	b	Comments
Hill	[8]	≥ 20	--	--	≤ 6	<b	>t-2d	Ductile Metals
Lee	[13]	8	8.6	1.1	3.3	0.070	0.188	Rubber modified PS
Barsom	[24]	2.7	1.6	0.6	2.2	0.060	0.375	Steels
Clausing	[25]	4.0	2.5	0.6	5.0	0.080	0.25	Steels
Higuchi et al.	[14]	Hill's constraints implied but not given						Annealed PC
Ellington	[27]	12	12	1.0	2.9	0.080	0.25	Copper and brass

tensile specimen develops necking at 54°44' to the tension axis when the metal is nearly isotropic. The 30° and 75° notches were included to provide more data points. The 55° notch was provided for a check on the correspondence of this notched condition to the uniaxial values in this "nearly isotropic" as-extruded polymer. The yield locus for the as-extruded notched tensile data for the 0.5% strain offset is shown in Figure 29 normalized to both the X1 uniaxial data and the 55° notched data. In this case the results are somewhat inconclusive since the 75° and 90° points normalized to the uniaxial data (ignoring the 55° pt) suggest a softer locus than the Von Mises Criterion while the same data normalized to the 55° point suggest a slightly harder locus than the Von Mises. Approaching the 1.0% offset from the 55° normalization produces Figure 30 which can be roughly interpreted as approximating the Von Mises Criterion. The 2.5% offset data normalized to the 55° point is shown in Figure 31 which strongly suggests a Von Mises material with the addition of fourth quadrant information (θ = 30°). Recorded on this same figure, the maximum load offset points again normalized to the 55° point (max. load) shows a slight softening in the first quadrant but a wild deviation in the fourth quadrant. This fourth quadrant behavior is recurrent in the as-extruded and annealed samples using the non-Hill constraints. The Lee type as-extruded case normalized to the uniaxial tensiles is

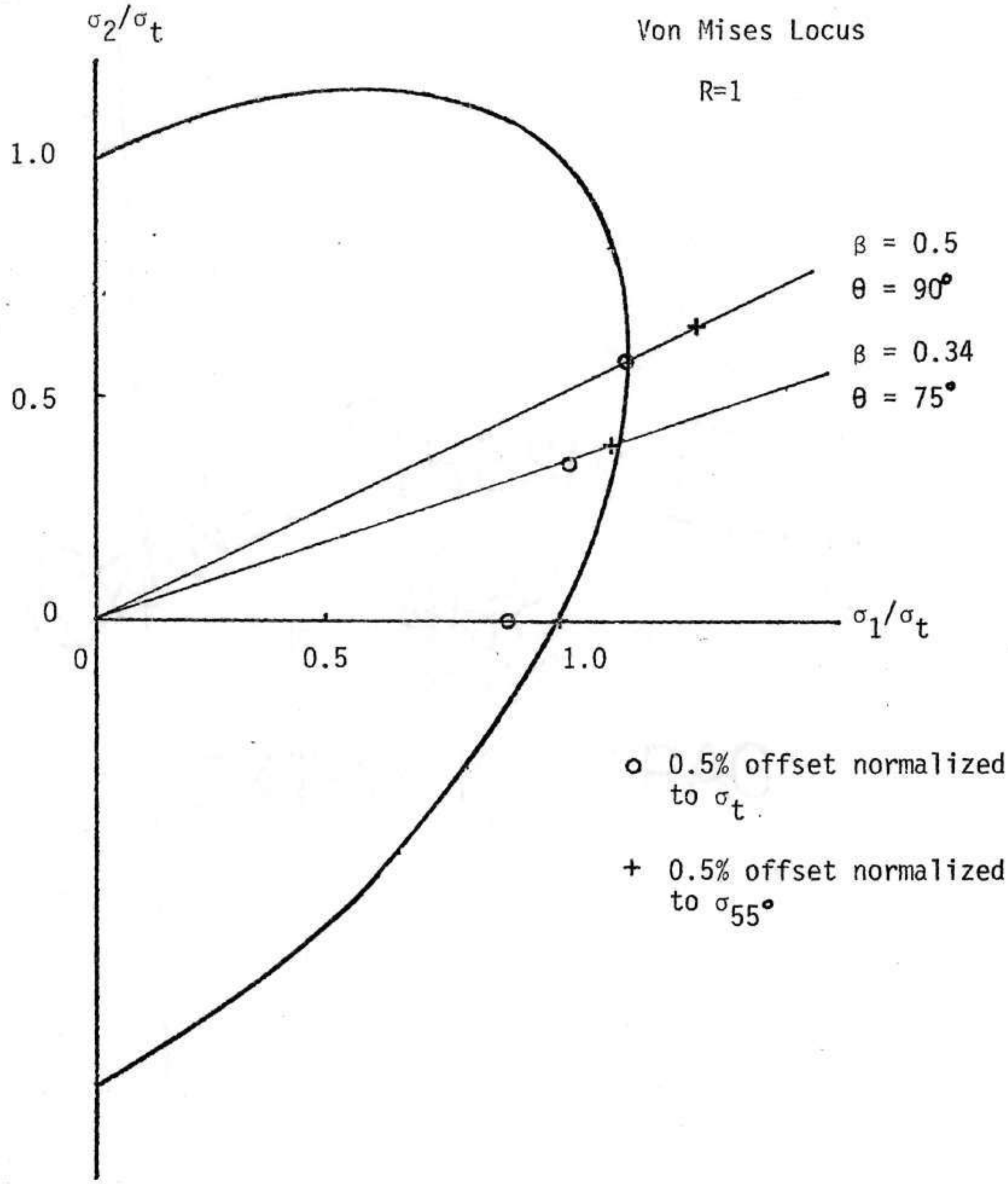


Figure 29. Normalized Principal Stress Plane Data for 0.5% Tensile Strain, As-Extruded PC, Hill's Constraints

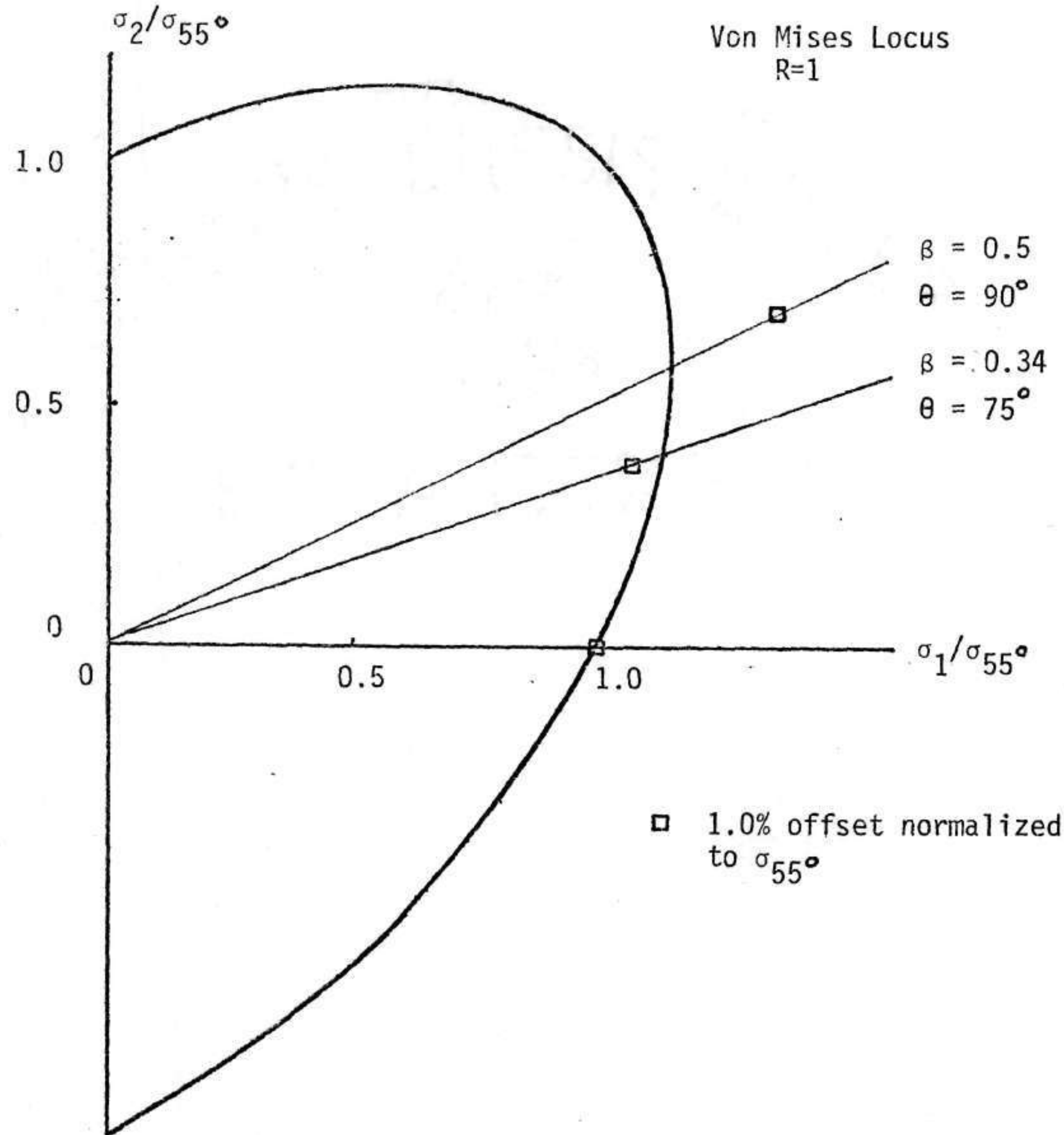


Figure 30. Normalized Principal Stress Plane Data for 1.0% Tensile Strain, As-Extruded PC, Hill's Constraints

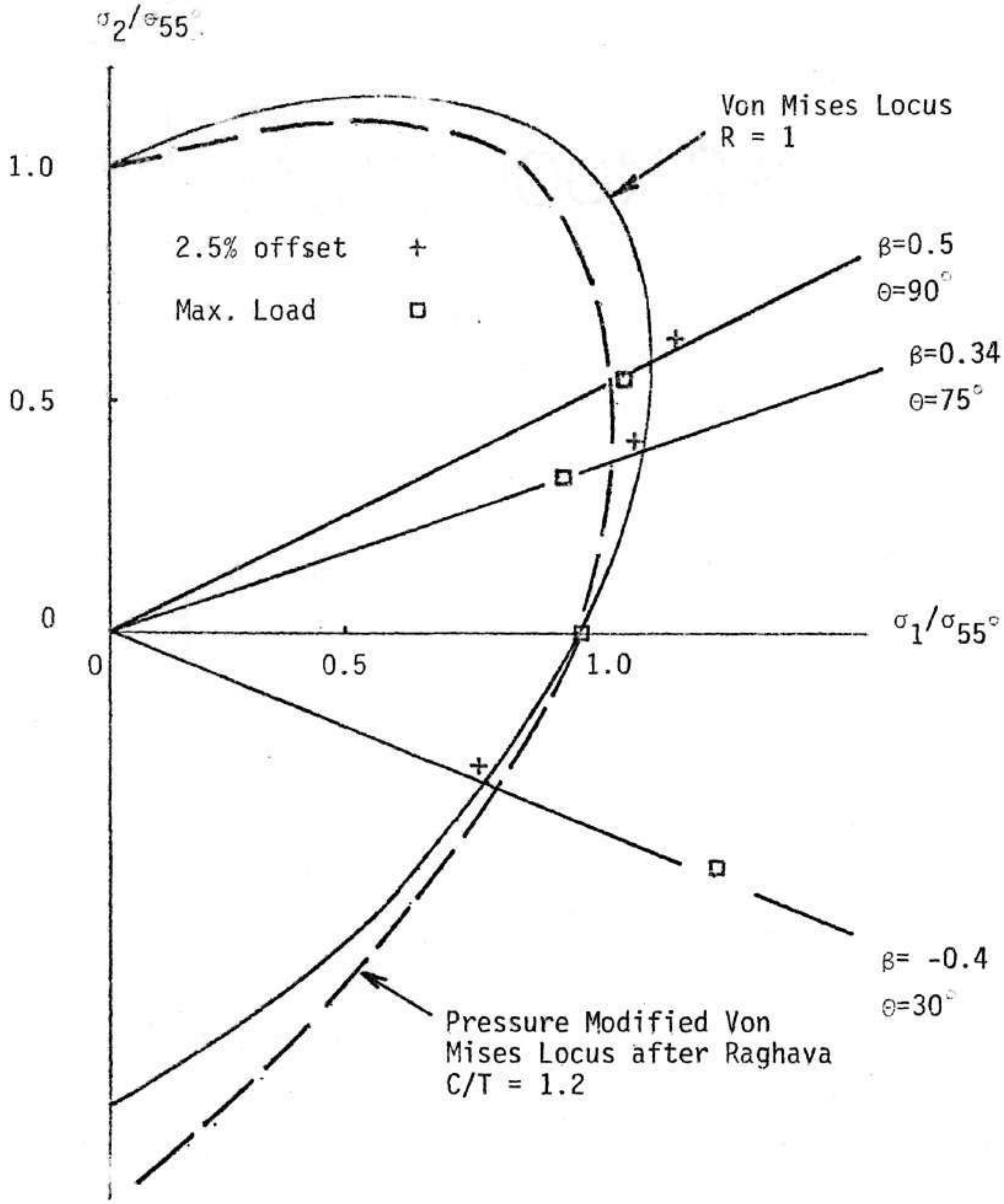


Figure 31. Normalized Principal Stress Plane Data for 2.5% Tensile Strain and Maximum Load Conditions -As-Extruded PC, Hill's Constraints

shown in Figure 32 for $\theta = 90°$ and $45°$ for the 0.5% and maximum load offsets. These four data points suggest a slightly softening pressure dependent criterion as did the maximum load Hill samples in the first quadrant. Figure 33 displays the limited notched tensile data for the annealed Lee type samples which indicate roughly Von Mises behavior in the first quadrant and deviant or pressure dependent behavior in the fourth quadrant.

Several of the hints at pressure dependent yield criteria seen in the notched tensile data were expressed by Raghava [22] in his work on PC. Figure 34 shows Raghava's pressure dependent modified Von Mises criterion compared to the original Von Mises form. Other investigations have found that polymers in general and amorphous glassy polymers in particular behave in a similar fashion. Raghava's work on both PC and PVC demonstrated a close correlation to a modified Von Mises with C/T = 1.3. He used rods in torsion and pressurized cylinders to obtain off axis data points. Lee [13] used notched PS tensiles similar to those of Hill that produced a pressure dependent yield locus in the first and fourth quadrant. Pae [26] investigated the yielding behavior of polypropylene (PP) and polyoxymethylene (POM) in a wide range of complex triaxial stress conditions. Again, at atmospheric pressure both polymers exhibited yield loci qualitatively similar to Raghava's results. Yield criteria for metals and polymers

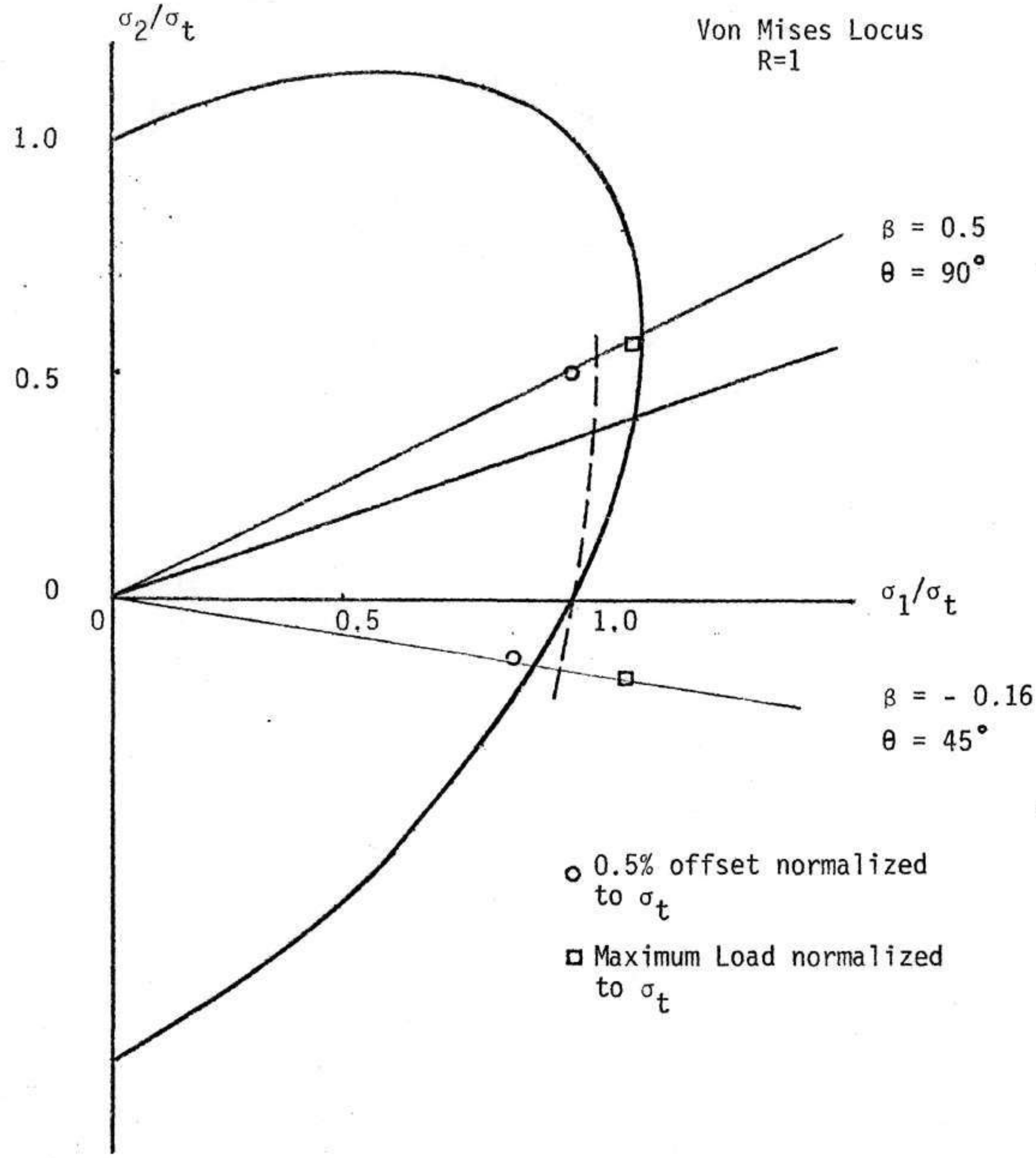


Figure 32. Normalized Principal Stress Plane Data for 0.5% Tensile Strain and Maximum Load Conditions As-Extruded PC, Lee Constraints